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HYDROCARBON CHEMISTRY.

A GENERAL DISCUSSION.

Monday, 17th, to Wednesday, 19th April, 1939.

THE SEVENTIETH GENERAL DISCUSSION of the Faraday Society was held in the Metallurgy Theatre of the Imperial College of Science, London, from Monday, 17th, to Wednesday, 19th April, 1939.

The subject was considered under the following heads:—

Part I. Homogeneous Thermal Reaction of Hydrocarbons.

Part II. Catalytic Reactions of Hydrocarbons.

Part III. The Mechanism of the Technical Synthesis and Transformation of Hydrocarbons.

- (a) Reactions of the Fischer-Tropsch Process.
- (b) Hydrogenation Reaction of Coal and Lignite.
- (c) Ring Closure and Isomerisation.
- (d) Combination of Saturated Hydrocarbons and Olefines.

Part IV. Olefine Polymerisation :

- (a) Dimerisation.
- (b) Lubricants (Medium Molecular Weight).
- (c) Plastics (High Molecular Weight).

The President (Professor E. K. Rideal) occupied the Chair throughout the meeting. By the courtesy of the Rector, members and visitors were accommodated at the Imperial College Hostel, where the Guest Night Dinner was held on Tuesday, 18th April.

At the inaugural meeting the President welcomed the overseas guests, members and visitors, as follows:—

Prof. E. Abel (*Wien*), Monsieur Barbière (*Paris*), Dr. A. Engelhardt (*Frankfurt a.M.*), Dr. W. F. Faragher (*Philadelphia*), Dr. H. Fromherz, (*München*), Dr. J. Guéron (*Strasbourg*), Prof. M. de Hemptinne (*Louvain*), Dr. H. Hoog (*Amsterdam*), Prof. G. Hugel (*Strasbourg*), Dr. T. Iredale (*Sydney*), Dr. W. Jost (*Leipzig*), Dr. J. C. Jungers (*Louvain*), Dr. and Frau L. Küchler (*Göttingen*), Dr. M. Mathieu (*Paris*), Prof. W. Mund (*Louvain*), Dr. J. Overhoff (*Amsterdam*), Dr. A. J. van Peski (*Amsterdam*), Dr. M. Prettre (*Lyon*), Dr. G. Salomon (*Delft*), Dr. G. R. Schultze (*Berlin*), Dr. J. Smittenberg (*Amsterdam*), Dr. J. Verheus (*Amsterdam*), Prof. and Mrs. H. I. Waterman (*Delft*), Dr. J. P. Werre (*Amsterdam*), Prof. E. C. Williams (*California*).

After the Introductory Paper had been presented by the President, the various reports and papers, which had been circulated in Advance Proof, were discussed in appropriate groups.

At the conclusion of the meeting votes of thanks were accorded to Sir Henry Carpenter and his staff at the Metallurgy Theatre, to the Rector of Imperial College, to Dr. H. J. Emeléus, to the authors of papers and translators, to the organising committee, as well as to the overseas members and guests for their attendance, and to the President for the courteous way in which he had conducted the meeting.

The Report of the meeting, including all the papers contributed, together with the discussion thereon, appears in the following pages.

HYDROCARBON CHEMISTRY.

Introductory Paper.

By ERIC K. RIDEAL.

The chief interest in hydrocarbon chemistry in the past was confined to problems connected with the separation and purification of various fractions from natural crude oils suitable for fuels for light and heavy engines as well as for lubricants. With increasing technological demands based upon rising octane and cetane numbers as well as increasing piston speed and higher pressures in bearings the problem of synthesis of suitable hydrocarbons has arisen in a more acute form. Apart from the needs of the automobile industry the various hydrocarbons are likely to become of increasing importance since they can serve as the raw materials of a number of the newer chemical industries, an economic and scientific field which is as yet almost virgin soil.

The problem can be approached from two different standpoints, we may enquire how we may transform a relatively unsuitable hydrocarbon fraction into another more suitable one, or how we may synthesise from coal the desired hydrocarbon, this latter method being naturally especially attractive to those countries without sources of natural oil but endowed with coal deposits.

Whilst the technical development of some phases of hydrocarbon chemistry has already attained a very high standard, the mechanism and the theory of the reactions involved are by no means clear, and indeed there are many quite definite divergences of opinion as to the interpretation of experimental data. It is the purpose of this discussion to develop the subject in such a manner that these differences of view may be given full expression so as to draw the attention of those academically inclined to the wide variety of problems, both theoretical and experimental, implicit and explicit which await solution in hydrocarbon chemistry.

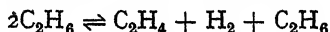
Thanks chiefly to the experimental work of our American colleagues, the free energies and heats of formation of a wide variety of hydrocarbons are now known with some accuracy. Accurate data on the specific heats, especially at more elevated temperatures, are, however, still badly needed. Nevertheless, it is possible to arrive at some idea of the equilibria in a number of reactions involving the hydrocarbons. In the homogeneous thermal reactions we require a knowledge both of the elementary steps and of the energies of activation involved. The electronic structures, the possible form of the transition complexes, the extent of resonance in conjugated systems, calculations of activation energies, e.g. between hydrogen atoms and the simpler hydrocarbons or between two dienes and the stability of radicals, are all problems which have received some attention from the theoretical chemist, and the first four papers are devoted to certain aspects of this method of approach.

The remaining papers in Part I give us an account of some of the views held on the homogeneous thermal reactions of the hydrocarbons,

the basis of the thermal cracking process. It is now generally agreed that these reactions are chain reactions in the sense that reaction initiated by one molecule brings about the reaction of a number of others through a radical chain before the chain is terminated. I believe that Professor F. O. Rice was the first to emphasise the essentially chain-like character, already accepted for processes of oxidation of the thermal cracking processes.

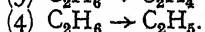
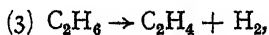
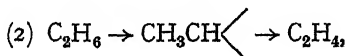
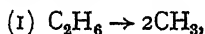
That chain reactions can play a part in decomposition can readily be demonstrated by insertion of suitable reaction centres or radicals produced either by the thermal or photochemical decomposition of substances like diazomethane, lead tetraethyl, or formed by oxidation of a small quantity of the hydrocarbon by the admission of a small quantity of oxygen or a peroxide. The average chain length can be determined, as was first shown by Professor Hinshelwood, by the use of nitric oxide, or from the extent of decomposition effected for each radical introduced. Whilst these views are generally accepted, there is a far greater difference of opinion when the actual nature of the chain system in any particular case is under consideration.

For example, in the decomposition of ethane to methane, carbon and hydrogen, a number of different processes have been proposed. Thus the initiation of the chain may be due to a reaction taking place at a wall or to a bimolecular gas reaction. By some it is believed that the chain initiation is not a radical formed in one of these ways, but the view has been advanced that a primary reaction of the type



takes place, and it is from the ethylene that the chain initiating radical is formed.

With ethane, protagonists are joined for the following different types of chain initiating radical:—



Radicals such as methylene can readily be produced by suitable chemical reactions, but whether these, in addition to or in lieu of methyl, are produced by the thermal decomposition of methane is still a matter of controversy. Belchetz and I concluded that we had obtained evidence for the former radical, but this is disputed by Rice.

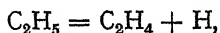
On the assumption that —CH_3 is the initiating radical produced from ethane



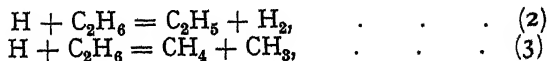
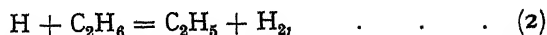
we note that one of the essential steps in the chain mechanism is the dehydrogenation of the hydrocarbon by the free radicals produced during the primary reaction, e.g.



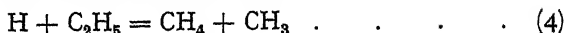
The ethyl radical then breaks up to yield a hydrogen atom



which can then attack further hydrocarbon molecules. Here two reactions are possible



We must not forget, however, that reactions of the type

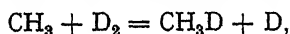


may take place, and that in addition a building up of hydrocarbons can take place by the interaction of radicals



To sort out these various methods of chain propagation and breaking evidently requires very careful analysis.

Finally, we may note that in the interaction of hydrogen or deuterium atoms with methane, which occurs at temperatures above 200° C. with an energy of activation of some 14 kg. cal. according to the reaction $\text{D} + \text{CH}_4 \rightarrow \text{CH}_3\text{D} + \text{H}$, we may also have $\text{D} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HD}$ with an additional reaction involving molecular deuterium



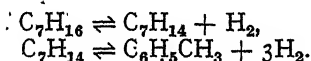
and so far the characteristics of these latter reactions have not been measured. The thermal decomposition of the aromatic hydrocarbons takes place at higher temperatures than for the aliphatics; it is interesting to note that Dr. K  chler finds that these decompositions are homogeneous, and that ring fissure follows such a relatively simple scheme.

Part II deals with the catalytic reactions of the hydrocarbons. Since such catalytic processes operate at low temperatures and permit of more selective control in the nature of the products than the purely thermal reactions, it is evident that increasing use will be made of them. Three important reactions take place in these catalytic processes, dehydrogenation, hydrocarbon degradation by carbon carbon fissure and ring closure. Any mechanism which is advanced for the interpretation of the catalytic formation of olefines and hydrogen from a saturated hydrocarbon must be able to permit of a satisfactory formulation of the reverse process of hydrogenation. Investigation of the catalytic interaction of deuterium with olefines has revealed that an exchange reaction proceeds simultaneously with the addition reaction. Here two divergent views have been expressed; in one the view is held that the olefine undergoes chemisorption with the simultaneous loss of a hydrogen atom prior to the addition of one of deuterium. On the other view, there is a primary addition of a deuterium atom to a chemisorbed olefine to form a half hydrogenated complex. In my laboratory this concept has been developed to interpret the chief reactions induced in the hydrocarbon hydrogen system in the presence of hydrogenating catalysts, and some results are given in the present papers. More information is required on the nature of the process of adsorption of a saturated hydrocarbon on a dehydrogenating catalyst. We are uncertain whether the process requires a high or small energy of activation, whether adsorption is due to interaction with chemisorbed hydrogen, and under what conditions the adsorbed hydrocarbon undergoes dehydrogenation to an olefine, to the half hydrogenated state, or to a number of degraded residues. Our own experience leads us

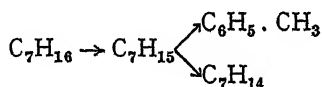
to the view that chemisorbed hydrogen plays a large part in these reactions. Alternative mechanisms are expressed in the communications by Professor H. S. Taylor and Dr. J. Turkevich and Drs. A. and L. Farkas and clearly much more experimental work is still required to elucidate the details of mechanism. We must congratulate Professor Taylor and Dr. Turkevich on the embrasive character of their communication.

Three papers are devoted to the technical synthesis of hydrocarbons, two to the Fischer Tropsch and one by Dr. Pier to the coal hydrogenation process. It will be seen from the first two papers that a commencement at any rate has been made to understand the steps in the mechanism which permit us to build up long hydrocarbon chains from water gas.

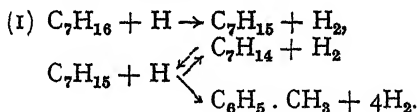
The important subject of ring closure to produce aromatic compounds from saturated straight chain hydrocarbons is discussed in three papers. Here again we note a divergence of view as to the mechanism. According to some investigators, notably Dr. Hoog, Verhuis and Zuiderweg the mechanism proceeds through an olefine equilibrium in the following manner, *e.g.*,



Mr. Pilkethly and Dr. Steiner, however, advance experimental evidence for the half hydrogenated state as being the active intermediary, a view which I have already referred to. The reaction scheme can, on this view, be written



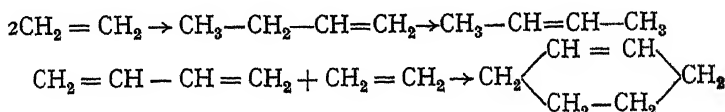
or on the assumption that the energy of activation is lowest for the reaction in which chemisorbed hydrogen takes part



Drs. Dunstan and Birch give us a brief survey on some of the problems arising out of one of the most interesting reactions in hydrocarbon chemistry, *viz.*, the catalytic addition of an olefine to an iso-paraffin. It is well known that a variety of catalysts, including boron trifluoride, aluminium chloride or sulphuric acid of suitable concentration will bring about this reaction at the low temperature necessary and with appreciable velocity. The reactivity of the hydrogen atom in tertiary hydrocarbons is remarkably high, and it is hoped that a theoretical attack on this problem may be made. Much more information is required as to the actual mechanism of this reaction. It is clear that not only can addition take place but a subsequent molecular rearrangement can occur similar to the conversion of *n*-heptane \rightarrow isoheptane. Whilst it is generally assumed that the conditions necessary for such a rearrangement are those in which olefine can be produced, this observation does not provide us with any clue as to the course of events in which apparently carbon carbon linkages are broken.

The last section of the discussion is devoted to the problems arising

out of the polymerisation of olefines. The formation of dimeric molecules is already important technically as a source of fuel. We are generally interested in olefines, diolefines, or mixed olefines, *e.g.*,



and cyclisation followed by dehydrogenation results in the production of aromatics.

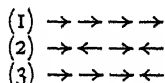
The process of growth of macromolecules of hydrocarbons is now beginning to attract especial interest. Whilst those of medium length find use as lubricants, noted by Professor Hugel, the successful technical development of polymers of butadiene, isoprene, styrene and ethylene for use in the plastic industries indicate how far technology has outstripped pure science in this field.

The two important hydrocarbons which can readily undergo macromolecular condensation are the olefines and the diolefines. It is evident in the case of ethylene, for example, that two types of chain growth can be visualised, these may be depicted as follows:—

1. $\text{CH}_2=\overset{\text{X}}{\text{CH}_2}+\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$.
2. $\text{CH}_2=\text{CH}_2+\text{X} \rightarrow \text{CH}_2\text{X}-\text{CH}_2-\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2\text{X}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$

In the first case polymerisation is only possible when a transfer of a hydrogen atom from molecule to molecule occurs. When this is not possible no polymerisation of this type is obtained. In the second case we initiate the process by forming a free radical by addition of a monovalent group such as H, Hg, CH_3 , or CH_3CO , to a molecule of the olefine, and subsequent growth occurs by the free radical mechanism. Both these types of chain growth have been experimentally realised.

In the case of an unsymmetric olefine, *e.g.*, $\text{CH}_2=\text{CHR}$, indicated by \rightarrow , several different types of polymers may be visualised, these may be regarded as



in which the first two represent an ordered array of molecules and the last a haphazard distribution (or a distribution partly influenced by energetics and partly by a steric factor). The diolefine system is evidently much more complicated in that a series of different possibilities are open.

On the assumption that polymerisation follows a quasi-diene reaction course we anticipate that the polymer produced would be a straight chain, one with all the double bonds in the chain. This is not found to be generally the case, as cross linkage is not an infrequent occurrence. Four papers are devoted to different aspects of such polymerisation processes.

PART I.—HOMOGENEOUS THERMAL REACTION OF HYDROCARBONS.

THE STRUCTURE AND ENERGIES OF SOME HYDROCARBON MOLECULES.

BY J. E. LENNARD-JONES, AND C. A. COULSON.

Received 20th March, 1939.

1. Molecular Orbitals and Resonance.

Most of the working rules of valency have now been given a definite, formal, and quantitative interpretation in terms of quantum mechanics. The underlying principles are the same as those which have elucidated the electronic structure of atoms and the experimental facts concerning their emission and absorption of light. The application of these principles to molecules has shown that the wave-patterns to be associated with electrons partake of the symmetry of the nuclear framework. Electrons in diatomic molecules, for instance, have a bi-nuclear character, whereas those in isolated atoms are localised about one nucleus. The latter are called *atomic orbitals* and the former may be described as molecular or *diatomic orbitals*. There is every indication that electrons in such orbitals have a finite probability of being associated with both atomic centres. It is not possible to draw a sharp distinction between the electrons in a molecule which are localised and those which are not. It is a matter of degree. But broadly it may be said that the inner electrons remain *monocentric*, while the outer unpaired electrons lose their localised properties in molecular formation and become, as it were, *polycentric* in character.

The extent to which electrons are shared between the various atoms differs from molecule to molecule. Just as it is not possible to draw a sharp distinction between atomic orbitals and diatomic orbitals, so it is not possible to say with precision how far an electron is localised between two atoms only and how far it is to be associated with others. Again it is a matter of degree. Strictly all electrons in a molecule, however large, should be regarded as belonging to the whole of the nuclear framework and described in appropriate general terms. But it is found in practice sufficiently accurate to consider some molecular orbitals as localised between two centres only, while others are of a more extensive kind.

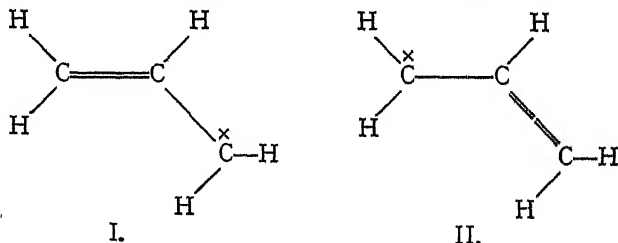
In general, it may be said that each normal single link in a molecule consists of a pair of electrons in a localised diatomic orbital, having opposite spins. Normal double links contain one pair of electrons in one kind of diatomic orbital, and another pair in another kind of diatomic orbital. In triple links there is a third pair of electrons in still another orbital. Theory agrees with experiment in assigning to normal single links the property of axial symmetry, so that there is no restriction, on this account, to free rotation about the link joining the two atoms.

The second link in a double bond does not in general possess this symmetry. It has instead a plane of symmetry passing through the line joining the two centres.* The effect of this is to restrict the relative rotation of two groups forming a double bond.

So far the theory may be said to confirm the rules and ideas prevalent in chemistry before the application of the wave theory of matter. But it is in the treatment of double and triple bonds, particularly when there is conjugation, that something new emerges.

In a conjugated hydrocarbon chain, bonds are usually described as being alternately single and double. From the theoretical point of view this description is not adequate, and in building up these molecules it is better to assign all the single bonds first. There is then one electron left over at each carbon atom. These could be assigned to a series of isolated double bonds, as is usually done in the normal chemical structural formula; but this would be tantamount to assuming that the bonds are localised, and closer examination of the electron wave-patterns does not justify this procedure. We cannot enter here into the details, but it may be said that these electrons are to be considered as a whole. They form a class different from the rest, because of their different symmetry properties. Their wave-patterns are similar to each other but different from the others. Sometimes they are called π -electrons¹ and sometimes *mobile* electrons,² because of their close similarity to the conduction electrons in metals. They cannot be regarded as localised in the same sense as electrons participating in a single bond, nor can they be paired according to their spins in a unique way to correspond to any one conventional structural formula. In dealing with them according to the method of molecular orbitals, each electron is assumed to move in the field of the nuclear framework and all the other electrons, and is allotted to a polycentric orbital embracing all the carbon atoms which are conjugated together, in conformity with the Pauli Principle.

Thus in the allyl radical, for example, it is possible to assign two alternative structural formulæ I and II, according as the unsaturated



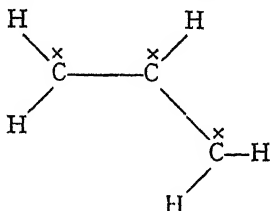
valency is associated with one or other of the terminal atoms. Another method of writing this radical is given in III, in which the mobile electron at each carbon is denoted by a cross (after Huckel). The orbitals to which these electrons are assigned, however, are not localised atomic orbitals, as might be suggested by the crosses, but may be described as tricentric; and are characterised by a certain wave-length along the chain. They are analogous to the vibrations of three equal particles equally spaced along a string. In one mode of vibration (the

* We refer here to the probability pattern and not to the wave function itself, which is anti-symmetric with regard to a plane.

¹ E. Huckel, *Z. Physik*, 1931, 70, 204; 1931, 72, 310; 1932, 76, 628.

² Lennard-Jones, *Proc. Roy. Soc., A*, 1937, 158, 280.

fundamental) all the particles move up and down together in phase; in another the central particle remains fixed while the other two are opposite in phase, one being up while the other is down. So there is one orbital which has no nodes, another which has one node at the central carbon atom—and so on.



III.

By the de Broglie relation, the momentum of a free electron is inversely proportional to the wave-length ($p = h/\lambda$), and the kinetic energy to the square of the wave-length. It is in accord with the relation (though a generalisation of it), that the kinetic energy of the wave-pattern with no nodes (the "fundamental") is less than that with one node, and that its total energy (kinetic plus potential) is lower than the rest. Now an orbital confined to two carbon atoms may be regarded as having wave-length of (roughly) the distance between them, and so the kinetic energy associated with such an electron is higher than with the fundamental tricentric orbital just considered. It follows that an electron in the fundamental has a lower energy content than one in the normal double bond. When we sum for all the electrons in the allyl radical, the net result is that its energy in form III is less than in either I or II. The difference between the two is called the *resonance energy*. The calculated value proves to be about 15 kcals. In general, the resonance energy is the difference between the actual energy of a system and the energy which it would have if all the bonds were localised as suggested by the orthodox method of drawing them. (Extensive calculations of resonance energies, using purely experimental values for the heats of combustion, have been made by Pauling and Sherman.)³

There is another method of calculating this effect, which has been used extensively by Pauling and his collaborators, and which applies in those cases where there are alternative methods of drawing the bonds. Each chemical bond-picture is represented by a wave function and the state of the molecule is described by a linear superposition of all those wave functions which are independent (the method of canonical structures). The properties of the molecule can then be defined and interpreted in terms of the individual structures. The energy of the resulting hybrid structure proves to be lower than that of any single one of the structural formulæ, even that which would appear to be the most stable.

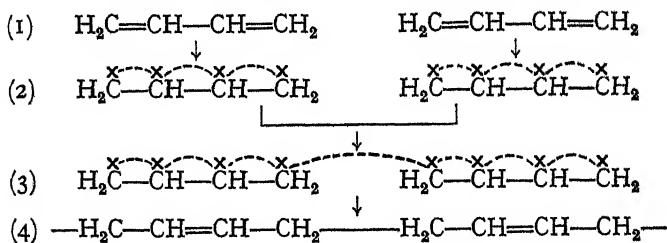
In the allyl radical the two bonds have been shown to be equal in length⁴ and to be slightly longer than a double bond. The link may be described by a number between one and two, and regarded as a bond of fractional order. This is found to be the case for all conjugated systems. The links are neither single nor double, but partake of the properties of both.

In this paper we shall be concerned mainly with the effect of resonance on energy content and on interatomic distances, but it is to be anticipated that other properties will be affected as well. The molecular character of the mobile electrons will permit the ready transmission of influences from one part of a molecule to another and so affect its reactivity.

³ Pauling and Sherman, *J. Chem. Physics*, 1933, 1, 606.

⁴ Coulson, *Proc. Roy. Soc., A*, 1938, 164, 383.

The interaction of the mobile electrons may take place even between one molecule and another, and help to form a temporary union by which other transformations take place. Thus, in the example shown between two butadiene molecules, given first by two conventional



formulae, and then diagrammatically by mobile electrons, we have in (3) a fusion of the two molecules, resonance taking place across the two ends; finally there is a rearrangement of the bonds, and the formation of a longer chain. In this way the phenomenon of resonance may often be an important factor in polymerisation.*

Another effect to be anticipated in molecules as a result of resonance is a modification of the restriction to rotation about the links, that round a "normal" double bond being reduced, and that round a "normal" single bond being increased. The magnitude of this has not yet been evaluated but some idea of its value may be inferred from the resonance energy. Thus in butadiene the resonance energy is about 5000 cal. per g. mol., and the central link is shortened to a value half-way between a normal single and double link. In this case the resonance energy must give an upper limit to the energy required to cause rotation about the central "single" link. (This calculation, of course, neglects possible steric hindrances due to interactions between other atoms further apart than the carbon atoms which form the "single" link.)

The change of energy and of carbon-to-carbon distances will cause a modification of the vibrational frequencies of its absorption spectrum. An experimental investigation of the frequencies to be assigned to the relative movement of carbon atoms in some of the simplest conjugated hydrocarbons would provide useful theoretical information about the forces operative in those links. The theoretical treatment in a simple case has already been indicated by Coulson.⁴

In the case of ring compounds the mobility of the "conjugated" electrons profoundly alters the magnetic properties. The high diamagnetic susceptibility about certain molecular axes in benzene and other molecules of a similar type has already received a preliminary interpretation in terms of molecular orbitals by Pauling and London. The physical nature of the effect has been made clear by their investigations. It is to be anticipated that the high electric polarisabilities of these molecules in certain directions may be interpreted in a similar way.

2. Calculations of the Energy.

We are now in a position to outline the calculations of the energies of these unsaturated molecules. This energy will depend upon the lengths of the various links (which we may call x_1, x_2, \dots). The actual

* *Added in Proof.*—Prof. Kistiakowsky informs us that he has already considered a similar mechanism (*J. Chem. Physics*, 1937, 5, 682) using the method of electron pairs.

configuration will be that for which the total energy is a minimum. So if F is the total energy, to be regarded as a function of x_1, x_2, \dots, x_n , then the equilibrium state of the molecule can be calculated if we determine F for all values of x_1, x_2, \dots , and then choose these so that F is minimised; i.e., if we satisfy the series of equations

$$\frac{\partial F}{\partial x_1} = \frac{\partial F}{\partial x_2} = \dots = \frac{\partial F}{\partial x_n} = 0. \quad (1)$$

We have seen that the electrons in these molecules are of two types, those which comprise the σ -bonds (localised between a pair of neighbouring carbon atoms), and the mobile, or polycentric ones. Each of these will make its contribution to F , and if we suppose that F is measured from a zero in which all the bonds are pure single bonds, then it may be written

$$F = E + V. \quad (2)$$

E is the binding energy of the mobile electrons, and V is the energy required to change the σ -bonds from their natural lengths ($s = 1.54$ Å). This latter may be referred to as the "compressional energy" of the σ -bonds. (It may be noted here that the well-known calculations using valence-bond structures make no allowance for this compressional energy, and are correspondingly in error.) The calculations of E and V are quite separate; let us consider V first.

If we consider a bond whose final length is x_i , the energy required to compress it from the normal single-bond length s is $k_s(x_i - s)^2$, where k_s is the force constant of a single bond. This is the contribution to V which arises from the bond x_i . k_s has a value of approximately 2.48×10^5 dynes per cm., obtained from an analysis of the vibration spectrum of ethane by Sutherland and Dennison.⁵ If the bond is greatly compressed then a Morse curve should be used instead of the parabolic law. The final value of V is obtained by summing $k_s(x_i - s)^2$ over all the bonds.

The calculation of E , however, demands a knowledge of the various electronic levels of the molecule, and we are thus led to consider in more detail the motion of each individual mobile electron. Each one of these moves in a field due to the attraction of the nuclei, together with the repulsions due to the σ -bonds and all the other mobile electrons. The resultant of all this is a field $v(r)$, which ought strictly to be calculated by the method of the self-consistent-field. This is far too complicated at present, and we merely suppose that $v(r)$ is the sum of local fields, writing

$$v(r) = v_1(r_1) + v_2(r_2) + \dots + v_n(r_n). \quad (3)$$

Here r_1 is the distance of the electron from nucleus 1, etc., and for simplicity we suppose that all the local fields are equivalent. This latter assumption will not be exactly correct, as Pauling and Wheland,⁶ and Evans and Warhurst⁷ have shown, especially when one or more hydrogen atoms have been replaced by atoms of different electron affinity. However, if we are only concerned with hydrocarbons and there are no foreign atoms, this approximation is valid (but see § 6).

The wave function of one of these mobile electrons has to express

⁵ Sutherland and Dennison, *Proc. Roy. Soc., A*, 1935, 148, 270.

⁶ Pauling and Wheland, *J. Chem. Physics*, 1933, 1, 362.

⁷ Evans and Warhurst, *Trans. Faraday Soc.*, 1938, 34, 614.

the fact that the electron may be found on any of the carbon nuclei, and therefore we write it

$$\Psi = a_1\psi_1 + a_2\psi_2 + \dots + a_n\psi_n, \quad (4)$$

where ψ_m is the wave function that the π -electron would have if it were confined to nucleus m , and the a_m are constants which we choose in such a way that wave function (4) is as good an approximation as possible to a true solution of the wave equation.

It is assumed in the calculations that all the ψ_m are orthogonal to each other (*i.e.*, $\int \psi_m \psi_{m'} dv = 0$, if $m \neq m'$), and that the resonance integral β across all atoms that are not nearest neighbours is zero. The problem of finding the coefficients a_m and the energy E of the electron is then reduced to the solution of the determinantal equation

$$\text{Det} \{H_{rs} - E\delta_{rs}\} = 0, \quad (5)$$

in which

if $r \neq s$, then $\delta_{rs} = 0$, and $H_{rs} = \beta_{rs}$ = resonance integral between atoms r and s ;

if $r = s$, then $\delta_{rs} = 1$, and $H_{rs} = E_0$ = energy of the mobile electron when confined to one of the carbon nuclei.

This determinantal equation can often be solved fairly simply; but if necessary it can be done numerically, and the possible energy levels of the mobile electrons determined as functions of the internuclear distances. The Pauli Exclusion Principle only allows two electrons (with opposed spins) to each energy level that is non-degenerate, and four in cases of twofold degeneracy. So by addition we find the total mobile energy E as a function of the lengths of the links.

We have assumed in the above that we know the value of the resonance integral β for any length of link. In the earliest calculations β was taken to be a constant independent of the length, but Lennard-Jones² showed that this was not the case, since the energy of the two π -electrons in ethylene was just 2β ; 2β is therefore the energy difference between a pure double and a pure single bond, when each is extended or compressed to the required length. These energies can be found from a knowledge of the force constants of ethane and ethylene. We are thus able to determine the value of β as a function of the bond length and hence to calculate E as a function of these lengths.

We have now shown how to calculate both V and E of equation (2), and the fundamental relation (1) gives us a series of equations which define the lengths of the links and the total energy of the molecule. This series of equations is rather troublesome to solve, since there are as many equations as there are mobile electrons, and each equation involves the lengths of all the links. But a series of approximations, equivalent to an iterative process, usually converges quite quickly, and the lengths and total energies are determined.

In this way we can calculate the total binding energy of the molecule; also it is easy to calculate the binding energy that we should have obtained if we had taken one of the usual chemical bond-diagrams, and added separately for each single and double link. The difference between these two quantities is the resonance energy.³

3. The Order of a Bond.

An alternative, but closely related, method of treating these aromatic compounds has recently been suggested by Coulson.⁸ In this treatment we first deduce the order of a bond, and then we are able to use an empirical relation between order and length to infer its length. The conception of order of a bond was first used to interpolate lengths and energies by Pauling, Brockway and Beach,⁹ and later the method was improved and extended by Penney;¹⁰ both treatments, however, were from the point of view of resonance among canonical structures rather than the motion of the mobile electrons. We shall therefore follow the treatment of reference (8).

The order of a bond in an aromatic compound is the sum of two parts; the one part is of magnitude unity, and is provided by the fixed localised σ -bonds; the other part is contributed by the mobile electrons. If we call this latter part p , then the total order is $1 + p$. For a pure double bond (ethylene) $p = 1$, and for a pure triple bond (acetylene) $p = 2$; for a pure single bond, of course, $p = 0$. p depends upon the density of mobile electrons in the region between the two atoms that form the bond. Thus, if there is a large density of electrons on two neighbouring atoms, we shall expect that the bond between these two atoms is of a higher order than if the densities are small. This may be correlated with the individual wave-functions. For suppose that a given electron has a wave-function of the type

$$\Psi = a_1\psi_1 + a_2\psi_2 + \dots + a_n\psi_n,$$

and that it is normalised, so that

$$a_1^2 + a_2^2 + \dots + a_n^2 = 1. \quad (6)$$

This electron will make a contribution to all the bonds. If a_r is large, then the electron may be said to spend a certain large proportion of its time around nucleus r . Now the condition for a big contribution to the order of the bond between two neighbouring atoms r and s is that there shall be a large probability of finding the electron on nuclei r and s . Let us therefore define the contribution of this electron to the order of the bond $r-s$ as being the simple product $a_r a_s$; this quantity satisfies our required condition of being large only when a_r and a_s are separately large. Then the total mobile order p is the sum of contributions $a_r a_s$ from each mobile electron present, and may be calculated if the coefficients a_1, a_2, \dots, a_n of the wave function are known.

This definition of order is consistent with the usual definitions of double and triple bonds. It has another interpretation also, since it can be shown that a bond of mobile order p contributes an energy p (energy of pure double bond) + $(1 - p)$ (energy of pure single bond), each measured at the appropriate distance. Strictly, of course, the coefficients a_r should be evaluated at the equilibrium configuration, but it appears to be satisfactory if we evaluate them on the hypothesis that all the resonance integrals are equal. This greatly simplifies the calculations, since the solution of the secular determinant (5) is often complicated when the resonance integrals are unequal, but very much simpler when they are equal. Confirmation of the method is found

⁸ Coulson, *Proc. Roy. Soc., A*, 1939, 169, 413.

⁹ Pauling, Brockway and Beach, *J. Amer. Chem. Soc.*, 1935, 57, 2705.

¹⁰ Penney, *Proc. Roy. Soc., A*, 1937, 158, 318.

from the fact that the lengths predicted in this way agree to within 0.01 Å with those predicted by Penney,¹⁰ using resonance methods.

One other interesting deduction can be made from the definition of bond order as being equal to $a_r a_s$. The coefficients a_r which occur in the wave function (6) are by no means restricted to have positive values; in fact only in the "fundamental" orbital will all the a_r be positive. Consequently a given electron will sometimes give a positive,

sometimes a negative, contribution to a bond; this implies a strengthening or a weakening of the bond, due to the given electron, and suggests that it may be possible to predict which bonds will be most weakened in an excitation process; at present, however, no application of the theory along these lines has been made.

According to the above calculations, knowledge of the bond order can be used to determine the energy of a bond, and, by addition,

the energy of the whole molecule. It can also be used to predict bond lengths. If we draw a smooth curve through the points corresponding to single, double and triple bonds ($p = 0, 1, 2$), and through the points representing benzene and graphite (all the lengths of which are accurately known), we obtain a curve which we may call the order-length curve (Fig. 1). It is possible to read off from this any required length, once the order of the link has been calculated.

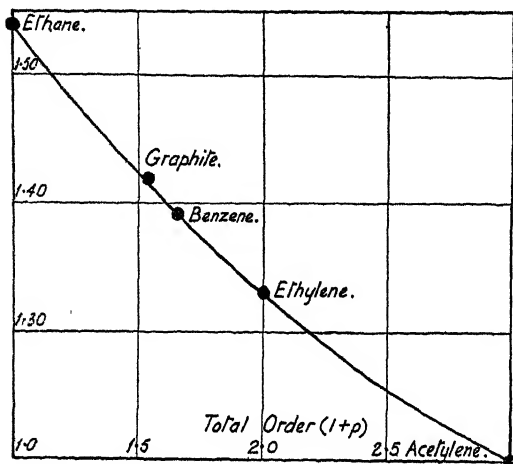


FIG. 1.—Relation between order and length of a C—C bond.

4. Results of Calculations of Order and Length.

Coulson⁸ has used the methods of the preceding section to obtain a general formula for the orders of the links in the conjugated chain molecules $C_{2n}H_{2n+2}$. If the links are measured in order from one end, then the fractional order of the r th link is

$$1 + \frac{1}{2n+1} \left\{ \operatorname{cosec} \frac{\pi}{4n+2} + (-1)^{r-1} \operatorname{cosec} \frac{(2r+1)\pi}{4n+2} \right\}. \quad (7)$$

The orders calculated from this formula are given in Table I; it is seen that the links do alternate in order, and hence in length, in a manner characteristic of the usual chemical bond diagram, but that these alternations become less and less appreciable as we go further along the chain into the centre of the molecule. With the infinite chain ($n \rightarrow \infty$), we find that fractional order

$$= 1 + p = 1 + \frac{2}{\pi} \left\{ 1 + \frac{(-1)^{r-1}}{2r+1} \right\}. \quad (8)$$

TABLE I.—ORDERS IN THE CONJUGATED CHAINS $C_{2n}H_{2n+2}$.

Molecule.	n .	End link x_1 .	x_2 .	x_3 .	x_4 .
Ethylene . .	1	2.00	—	—	—
Butadiene . .	2	1.894	1.447	—	—
Hexatriene . .	3	1.871	1.483	1.785	—
Octatetraene .	4	1.862	1.495	1.758	1.529

The lengths of the conjugated chains determined in the cases of $n = 1, 2, 3, 4$ are shown in Table II. The orders and the lengths of the infinite chain are given in Table III, from which it will be seen that there are

TABLE II.*—LENGTHS IN THE CONJUGATED CHAINS $C_{2n}H_{2n+2}$.

Molecule.	n .	End link x_1 .	x_2 .	x_3 .	x_4 .
Ethylene . .	1	1.33 ₀	—	—	—
Butadiene . .	2	1.34 ₅	1.43 ₂	—	—
Hexatriene . .	3	1.35 ₁	1.42 ₄	1.36 ₈	—
Octatetraene .	4	1.35 ₈	1.42 ₂	1.37 ₁	1.41 ₅

TABLE III.—LENGTHS AND ORDERS IN THE INFINITE CHAIN $C_{2n}H_{2n+2}$.

Link Number.	1.	2.	3.	4.	5.	6.	Asymptotic Value.
Order . .	1.849	1.509	1.727	1.566	1.694	1.587	1.637
Length . .	1.35 ₅	1.41 ₉	1.37 ₇	1.40 ₇	1.38 ₈	1.40 ₄	1.39 ₄

appreciable alternations in length up to the seventh from each end. (Compare also Penney, reference 10, page 321.) Similar calculations can be made for the cyclic molecules $C_{2n}H_{2n}$. As Wheland¹¹ has shown, these molecules are regular polygons, and their orders can be calculated.¹² The actual figures are given in Table IV, the orders

TABLE IV.—ORDERS AND LENGTHS OF THE CYCLIC MOLECULES $C_{2n}H_{2n}$.

Molecule.	n .	Order.	Length.
Cyclobutadiene . .	2	1.500	1.42 ₁
Benzene . .	3	1.667	1.38 ₈
Cyclo-octatetraene .	4	1.604	1.40 ₀
Cyclodecapentene .	5	1.647	1.39 ₁
Cycloduodecahexene .	6	1.622	1.39 ₈
—	∞	1.637	1.39 ₄

* In calculating the lengths of the links in this and Tables III, IV, and V, it has been assumed that the single link is exactly 1.540 Å and the double link exactly 1.330 Å. This is almost certainly not true, and the last figure in each length, written as a subscript, has no absolute significance; it is of interest, however, for comparing relative lengths of links.

¹¹ Wheland, *Proc. Roy. Soc., A*, 1938, 164, 397.

¹² Coulson (*in course of publication*).

being calculated from the formulæ

$$n \text{ even: order} = 1 + p = 1 + \frac{1}{n} \cot \frac{\pi}{2n}, \quad (9a)$$

$$n \text{ odd: order} = 1 + p = 1 + \frac{1}{n} \operatorname{cosec} \frac{\pi}{2n}. \quad (9b)$$

It is almost certain however, that only when $n = 2, 3$ or 4 is the molecule planar, and if it is bent out of a plane (as even cyclo-octatetraene may be) then the calculations do not hold without further correction, though they do indicate the approximate lengths.

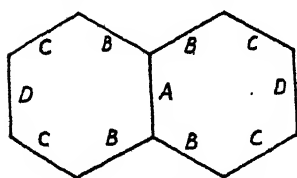


FIG. 2.—The links of naphthalene.

Another interesting case is the naphthalene molecule. As Fig. 2 shows, there are four essentially different bonds, and their orders and lengths are shown in Table V, due to Coulson.¹² None of these links differ by more than 0.005 Å from the lengths predicted by Penney,¹⁰ using

electron-pair methods. Similar calculations have also been used¹² to discuss the progressive hydrogenation of naphthalene.

TABLE V.—LINKS OF NAPHTHALENE.

Link.	A.	B.	C.	D.	Mean.
Order . .	1.518	1.555	1.725	1.603	1.622
Length . .	1.41 ₇	1.40 ₂	1.37 ₇	1.40 ₀	1.39 ₄

Penney and Kynch¹³ have discussed the molecules of phenylethylene, stilbene, and tolane. Using the notation of Fig. 3, the predicted lengths are as shown in Table VI. In each case the lengths of the link B have been measured experimentally by Robertson and Woodward¹⁴ and they agree excellently to within 0.01 Å.

Calculations have also been made by Coulson⁴ upon certain free radicals. In the radical C_5H_7 , for example, shown in Fig. 4, the lengths of the C—C bonds, in order, are

1.35, 1.39, 1.39, 1.35 Å.

Similar values are obtained for the higher members of this series $C_{2n+1}H_{2n+3}$. Such radicals tend to form dimers (at least this will

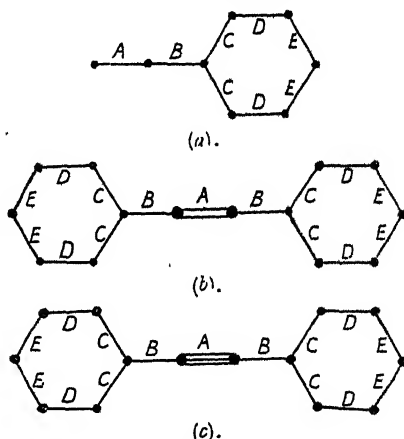


FIG. 3.—(a) Phenylethylene. (b) Stilbene. (c) Tolane.

¹³ Penney and Kynch, *Proc. Roy. Soc., A*, 1938, 164, 409.

¹⁴ Robertson and Woodward, *Proc. Roy. Soc., A*, 1937, 162, 568; 1938, 164, 421.

TABLE VI.—LENGTHS OF LINKS OF CERTAIN MOLECULES.

Link No.	A.	B.	C.	D.	E.
Phenylethylene .	1·34	1·44	1·37 ₄	1·37 ₇	1·37 ₄
Stilbene .	1·34	1·44	1·37 ₄	1·37 ₇	1·37 ₄
Tolane .	1·20	1·40	1·37 ₄	1·37 ₇	1·37 ₄

be true for the lower members of the series) and reasonable heats of dimerisation can be obtained.

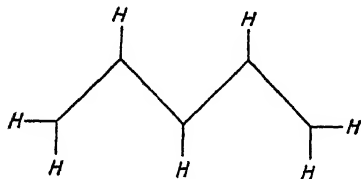
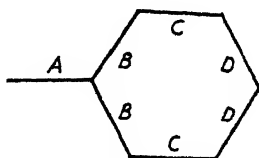
FIG. 4.—Radical C_6H_7 .

FIG. 5.—Phenylmethyl radical.

Penney and Kynch¹³ have also discussed the phenylmethyl radical $H_2C \cdot C_6H_5$. With the nomenclature of the links shown in Fig. 5, they find the distribution of lengths to be that of Table VII.

TABLE VII.—LENGTHS OF LINKS OF PHENYL-METHYL RADICAL.

Link.	A.	B.	C.	D.
Length .	1·38	1·41	1·38	1·39

5. Results of Calculations of Energy.

A large number of other calculations of the energy have been made, and comprehensive tables are given in two excellent reviews by Hückel.¹⁵ Unfortunately in all these cases no allowance has been made for a variation of lengths among the links, and although the results will be approximately correct, they need revision to allow for this. In Table VIII, however, are collected together the values which have been calculated when allowance for this variation has been made. The number in brackets after the energy value refers to the paper from which the result has been taken. In view of the experimental uncertainties in the true value of the energy of a single and a double bond, the resonance energies given in Table VIII cannot claim any great absolute accuracy; but their relative values, especially in homologous series, are almost certainly reliable.

6. Conclusion.

Certain criticisms of the methods reported above must be included in this report. In addition to essential difficulties due to uncertainties of the fundamental constants for the single and double bonds, we must mention the discussion of cyclobutadiene by Wheland,¹¹ who showed that in those cases where the molecular orbital method finds that the

¹⁵ Hückel, E., *Phys. Soc. Int. Conf. Physics*, p. 1, London, 1935, *Z. Elektroch.*, 1938, 43, 785.

highest occupied level is only partly filled (through having only one electron to occupy it, or through the existence of degeneracy, so that there are two or more space orbits with the same energy, and not all are filled), then it is often unreliable; this is because in its simplest form it fails to take account of the fine structure. Examples of such cases are the cyclic molecules $C_{4n}H_{4n}$ and many of the free radicals. No one, however, has so far estimated the error involved.

Another criticism relates to the effect of polar states. Sklar¹⁶ has shown that the polar states in ethylene make a very appreciable contribution to the energy, of approximately 5 kcal. Proper allowance is not made for this in any of the theories described in this paper, nor is it known to what extent polar states affect the energies of molecules

TABLE VIII.—RESONANCE ENERGIES (KCAL.).

Open Conjugated Chains $C_{2n}H_{2n+2}$.

Compound.	Butadiene.	Hexatriene.	Octatetraene.	Decapentene.
Formula . . .	C_4H_6	C_6H_8	C_8H_{10}	$C_{10}H_{12}$
Res. energy (calc.) .	5.4 (2)	11.4 (2)	17.1 (4)	22.3 (4)
	5.0 (4)	10.8 (4)	—	—
Res. energy (expt.) .	5 (3)	—	—	—

Condensed Ring Systems.

Compound.	Benzene.	Diphenyl.	Naphthalene.	1, 2 di-Hydro-naphthalene.	Cyclobutadiene.	Cyclo-octa-tetraene.
Formula .	C_6H_6	$C_{12}H_{10}$	$C_{10}H_8$	$C_{10}H_{10}$	C_4H_4	C_8H_8
Res. energy (calc.) .	30.2 (19)	65.4 (19)	52.6 (19) 63.3 (12)	34.2 (12)	0 (19)	18.8 (19)
Res. energy (expt.)	37 (3)	87 (3)	75 (3)	47 (3)	—	—

Free Radicals $C_{2n+1}H_{2n+3}$.

Compound . . .	C_3H_5	C_5H_7	C_7H_9	C_9H_{11}
Res. energy calculated relative to n double bonds . . .	15.4 (4)	25.5 (4)	33.0 (4)	40.2 (4)

other than ethylene and benzene. Calculations of a slightly different type on water by Coolidge¹⁷ and on methane by Voge¹⁸ indicate that the effect of polarity and ionicity is far from negligible.

The question of end-effects has not been adequately discussed; we have assumed that the potential $v(r)$ of equation (3), in which the mobile electrons move, is exactly the same around every one of the carbon nuclei. This, however, is only approximately true, since the end carbon atoms of a chain molecule such as $C_{2n}H_{2n+2}$ have three σ -bonds, two of which are C—H and one is C—C, whereas the internal

¹⁶ Sklar, *J. Chem. Physics*, 1937, 5, 669.¹⁷ Coolidge, *Physic. Rev.*, 1932, 42, 189.¹⁸ Voge, *J. Chem. Physics*, 1936, 4, 581.¹⁹ Lennard-Jones and Turkevich, *Proc. Roy. Soc., A*, 1937, 158, 297.

carbon atoms still have three σ -bonds, but only one is C—H and two are C—C. This means that there is an end-effect, the importance of which is not at present known.

It must, however, in fairness, be added that where correlation with experimental values is possible, excellent results are obtained. And some reliance may be placed upon the predicted lengths for the various links, since, as we have shown, the two essentially different methods of approach, either by resonance among canonical structures or by the use of the notion of mobile electrons, give almost identical predictions in most cases.

In conclusion it may be added that these problems are of considerable mathematical complexity; progress has been possible in the past through recognising: first, that the mobile electrons, because of their unique symmetry properties, can be dealt with separately; second, that the effect of the σ -bonds can be included through the concept of compressional energy; and third, that the unknown resonance integral can most easily be correlated with experiment in terms of certain force constants. It seems likely that further advances will be made, not by a direct frontal attack on the problem, but by attempting to interpret one molecular property in terms of another. Thus it may be possible to combine observations of apparently unrelated kinds into one theoretical scheme.

Summary.

A review is given of theoretical valence rules in molecules, and the structure of many hydrocarbon molecules is correlated with the motions of the valence electrons; these electrons are of two types, those responsible for single or σ -bonds, and those responsible for double or π -bonds. In many cases, such as conjugation of double bonds, these latter electrons must not be considered to be localised in any region, as would be suggested by the usual chemical bond-diagram, but must be considered mobile, free to move throughout the whole molecule. As a result, the energies, lengths, bond orders, resistance to twisting, electric and magnetic properties of these links are profoundly modified, and the nature of these modifications is outlined. Details of the calculation of energy, order and length are given, and tables are included of all those molecules for which results are available. Where comparison with experiment is possible, the lengths and energies agree excellently. Finally a criticism of the method is made, and possible improvements in the calculations discussed.

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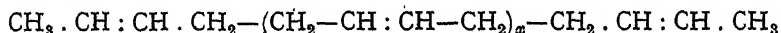
THE ACTIVATION ENERGIES OF REACTIONS INVOLVING CONJUGATED SYSTEMS.

BY M. G. EVANS.

Received 15th March, 1939.

The properties and reactivity of conjugated molecules form a field of study which is of particular interest and importance to the chemist. Molecules of this type show on the one hand enhanced thermochemical stability, while on the other hand they show in some of their reactions greater reactivity than do non-conjugated substances. For example the dimerisation of a diene occurs with an activation energy which is much less than that for the dimerisation of non-conjugated olefines. The addition of a 1 : 3 conjugated system to a double bond occurs in most cases with such ease that this reaction is a standard method in organic chemistry for detecting the presence of conjugation in a molecule.

Moreover, apart from the dimerisation reactions of dienes to yield six membered rings, conjugated molecules are known to polymerise to give compounds of a very high molecular weight for which structures of the type



have been suggested.

In recent years it has been possible to correlate many of the special properties of conjugated molecules with the rather special behaviour of the π electrons in these molecules.¹ In this discussion I wish to suggest that the reactivity of such molecules can be attributed to the same source as can the regularities of absorption spectra, the diamagnetic anisotropy of conjugated nuclear compounds and the enhanced thermochemical stability of all conjugated molecules.

The Method used for the Discussion of Reaction Energetics.

In previous publications² it has been emphasised that for many reactions a sufficiently close approximation to the potential energy surface for reaction can be obtained by constructing two intersecting potential energy surfaces. One surface represents the potential energy of all configurations with the bond assignment of the initial state, and the other surface that for the bond assignment of the final state of the reacting system. These two potential energy surfaces intersect in a continuous series of configurations, and the lowest energy along this line of intersection is for many reactions a fairly good approximation to the energy of the transition state for the reaction.

In terms of the ψ -functions representing the initial and final bond

¹ Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362; Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606, 679; Huckel, *Z. Physik*, 1931, **70**, 204; 1931, **72**, 310; 1932, **76**, 628; Lennard-Jones, *Proc. Roy. Soc., A*, 1937, **158**, 280, Lennard-Jones and Turkevitch, *ibid.*, 297.

² Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11.

assignments in the system the energy of these two surfaces can be expressed by

$$E_1 = \frac{\int \bar{\psi}_1 H \psi_1 d\tau}{\int \bar{\psi}_1 \psi_1 d\tau} = \Sigma Q^{(1)} + \Sigma_{ii} J_{ii}^{(1)} - \frac{1}{2} \Sigma_{ij} J_{ij}^{(1)}$$

$$E_2 = \frac{\int \bar{\psi}_2 H \psi_2 d\tau}{\int \bar{\psi}_2 \psi_2 d\tau} = \Sigma Q^{(2)} + \Sigma_{ii} J_{ii}^{(2)} - \frac{1}{2} \Sigma_{ij} J_{ij}^{(2)}$$

where $Q^{(1)}$ and $Q^{(2)}$ represent the coulombic integrals in the initial and final states, and $J_{ii}^{(1)}$ and $J_{ii}^{(2)}$ are the corresponding exchange integrals between the bonded electrons, and $J_{ij}^{(1)}$ and $J_{ij}^{(2)}$ those between non-bonded centres.

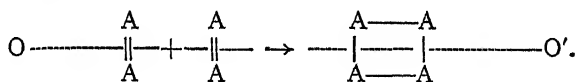
The true energy surface is a continuous one, and can be obtained from the two surfaces defined above by taking into account the resonance energy between the initial and the final states. This resonance energy $E_{12} \sim \int \bar{\psi}_1 H \psi_2 d\tau$ will only be appreciable in the neighbourhood of the intersection line of the two surfaces E_1 and E_2 , that is, for those regions for which $E_1 \sim E_2$.

The continuous lower energy surface is given by the lowest root of the secular equation

$$\begin{vmatrix} \int \bar{\psi}_1 H \psi_1 d\tau - E \int \bar{\psi}_1 \psi_1 d\tau & \int \bar{\psi}_1 H \psi_2 d\tau - E \int \bar{\psi}_1 \psi_2 d\tau \\ \int \bar{\psi}_2 H \psi_1 d\tau - E \int \bar{\psi}_2 \psi_1 d\tau & \int \bar{\psi}_2 H \psi_2 d\tau - E \int \bar{\psi}_2 \psi_2 d\tau \end{vmatrix} = 0.$$

In this treatment we shall first deal with the activation energies by the diabatic method, that is, by taking the cross-section through the two discontinuous surfaces which leads to the lowest point of intersection for the two surfaces and then we will discuss the resonance energy between the two states as an additional factor.

By way of illustration of the diabatic method let us deal with the imaginary reaction



The energetics will be studied for a reaction path in which the system maintains its symmetry about the O'O axis and the configuration can then be defined in terms of two co-ordinates, one along the OO' axis and the other at right angles to it. The type of potential energy surface which would be obtained for such a reaction is shown in Fig. 1, it is made up of two surfaces. Surface I for the system with the bond assignments of the initial state and surface II that for the system with the bond assignments of the final state.

A cross-section through the line XY where the molecules A_2 are infinitely separated gives the energy of extension of the two $\text{A}=\text{A}$ bonds perpendicular to the OO' axis. A cross-section through the line XZ on surface I gives the energy of interaction between two A_2 molecules along the OO' axis. This interaction energy is mainly repulsion energy, although at fairly large distances there will be an attraction potential between these two molecules arising from van der Waals forces. On the final state surface a section through the line AB yields the extension energy of the A_4 molecule perpendicular to the OO' axis, and a section through the line AC the extension energy of the A_4 molecule along the OO' axis.

The dotted line on this diagram represents the reaction path for the system, and the total energy changes involved can be divided up by taking a discontinuous section through the surface. The energy change along this section $XX'TA'A$ is shown in Fig. 2, and is made up of the

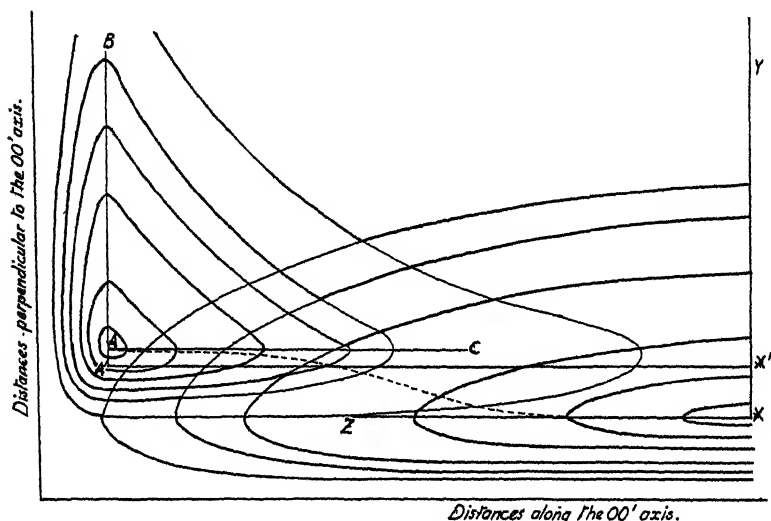


FIG. 1.

following terms:—

From X to X' . The energy of extending two $A=A$ bonds perpendicular to the OO' axis.

X' to T . The energy of interaction between two A_2 molecules along the OO' axis. This energy is chiefly repulsion energy.

T to A' . The energy change of extension of the $\begin{array}{c} A-A \\ | \\ A-A \end{array}$ structure along to the OO' axis.

A' to A . The energy of compression of the $\begin{array}{c} A-A \\ | \\ A-A \end{array}$ structure perpendicular to the OO' axis.

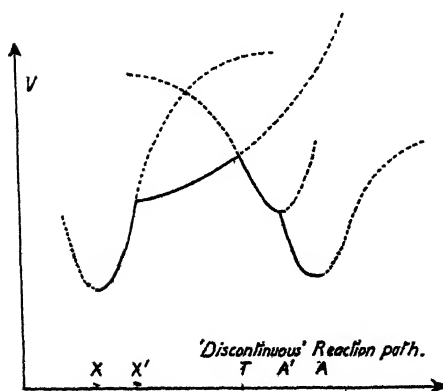


FIG. 2.

At the point T the initial state bond assignment and the final state bond assignment both have the same configuration and the same energy, and at this point an electron switch can occur and the system change over from the initial to the final state.

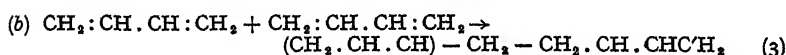
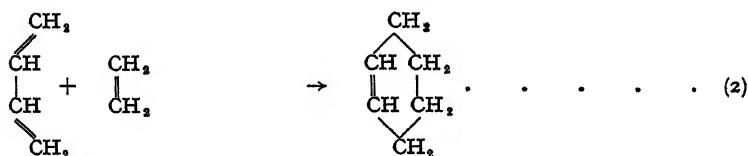
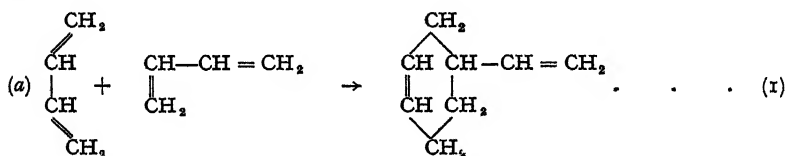
If, for the present, we neglect the resonance energy in the neighbourhood of this intersection point the following factors will contribute to the activation energy of reaction.

The activation energy will be reduced by :

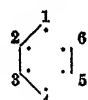
- (a) A small energy of distortion of the A=A bonds in the initial state.
- (b) A small repulsion energy between the two approaching A₂ molecules of the initial state.
- (c) A small energy of distortion of the bonds of the final state.
- (d) A high heat of reaction, that is, the formation of strong bonds in the final molecule.

Considerations of the Separate Factors Contributing to the Activation Energy.

The above considerations are quite general and will apply to all cases of dimerisation reactions but here we will deal chiefly with the dimerisation reactions involving conjugated molecules. These will be of two types:—



(1) The Repulsion Energy Between the Associating Molecules.

In the case of an association reaction involving the centres  the repulsion energy is given by

$$E = Q_{1,6} + Q_{4,5} - \frac{1}{2}J_{1,6} - \frac{1}{2}J_{4,5}$$

where the interaction between non-adjacent carbon centres has been neglected, and $(Q_{1,6} + J_{1,6})$ and $(Q_{4,5} + J_{4,5})$ are the bond energies between the carbon centres 1 and 6 and between 4 and 5 respectively. For the other type of approach of the two molecules the repulsion energy is, again neglecting the interaction between non-adjacent carbon centres,

$$E = Q_{4,5} - \frac{1}{2}J_{4,5}$$

Since Q is of the order of 10 to 15 per cent. of the total bond energy at any internuclear separation, it is clear that the repulsion energy to be overcome is much less in the "end on method" of attack than in the case of the "broad side on" approach of the two molecules.

(2) The Influence of the Heat of Reaction.

The heat of reactions involving conjugated molecules is determined by the change in the energy of the mobile π electrons and the change in the energy of the carbon skeleton. It has been shown by Lennard-Jones³ and his collaborators that a very good account of the energy and the configuration of conjugated systems can be given by considering the mobile π electrons to be moving in the potential field set up by the whole carbon skeleton. This molecular behaviour of the π electrons leads to the result that the system does not possess the energy nor the configuration of a system made up of double and single bonds. For example,³ in buta-diene the distances between the carbon centres $C^1-C^2-C^3-C^4$ are $r_{12} = r_{34} = 1.33$ Å and $r_{23} = 1.44$ Å as compared with $r = 1.32$ Å and $r = 1.54$ Å for the isolated double and single bonds respectively. The energy of the π electrons of the buta-diene molecule is -116.8 k. cal. as compared with -111.4 for a system of true double and single bonds. These changes in the molecular structure and energy arising from the behaviour of the π electrons influence two factors in those contributing to the activation energy. In the first place, during reaction it may be that the possibilities of resonance have been lost or created by a change in the number of mobile π electrons. For example, in reaction (2) the π electrons of buta-diene lose their mobility and become localised as the σ bonds between centres 1 and 6 and 4 and 5 and the double bond between centres 2 and 3.

The heat of reaction is given by the following terms :—

Loss of resonance energy of the butadiene molecule	= -5.4 k. cal.
The energy of breaking two $C=C$ bonds and forming two $C-C$ bonds	= -111.4 k. cal.
Energy of forming two $C-C$ bonds	= $+145.2$ k. cal.
Total energy change involved in the reaction	= $+28.4$ k. cal.

Similarly for, reaction (1) involving two buta-diene molecules each of which loses its resonance energy during reaction the heat change involved is $+23.0$ k. cal. This heat change computed from the theoretical values for the resonance energy and the bond strengths is of the right magnitude is seen from the value of 18 ± 3 k. cal. obtained for the heat of reaction of cyclopentadiene, from the differences between the activation energies for the association and reverse reactions.⁴

In the other type of dimerisation reaction to form a diradical, although the conjugated structure is lost and hence the extra molecular energy associated with the mobile electrons is lost, the diradical contains a structure of the same type as the allyl radical in which three π electrons are moving in the periodic field set up by three carbon centres. Coulson⁵ has calculated the resonance energy for the allyl radical as 15.4 k. cal., and hence the loss of resonance energy by the butadiene molecule is more than offset by the resonance energy in the radical. The heat of the reaction between an ethylene and a butadiene molecule is thus -18.8 k. cal. and for two butadiene molecules associating in this same way when two allyl-like groupings are formed the heat of reaction is -8.8 k. cal.

³ Lennard-Jones, *Proc. Roy. Soc., A*, 1937, **158**, 280; Penny and Kynch, *Proc. Roy. Soc., A*, 1938, **164**, 409.

⁴ Bamford, Kambata and Wasserman, *Nature*, 1937, **139**, 669.

⁵ Coulson, *Proc. Roy. Soc., A*, 1938, **164**, 383.

There is indirect evidence for this resonance energy of the allyl radical. It has been found possible in a semi-empirical way to account for the changes in activation energy of the reactions of sodium atoms with organic halides. The very rapid reaction, with an activation energy of 6.5 k. cal., found in the case of allyl chloride can be accounted for quite adequately by using the fundamental frequency of the CCl bond in allyl chloride and a resonance energy of the radical of 15.20 k. cal. Unless this resonance energy is taken into account the calculated activation energy is completely out of line with those computed for other compounds in which the radical possesses no resonance energy.

Reverting to the present discussion we find that although the repulsion energy favours the end on attack to form a diradical the heat of reaction favours the formation of a six membered ring. The unfavourable heat of reaction in the formation of the diradical is, however, greatly reduced by the formation of radicals which possess large amounts of resonance energy.

The Distortion of the Structure.

All these changes involving as they do the opening of double bonds and the formation of single bonds necessitate the distortion of the molecular framework during the course of reaction. For example, in the initial state of reaction (2) the distances are $r_{12} = r_{34} = r_{56} = 1.33$ and $r_{23} = 1.44$ Å while in the final state $r_{12} = r_{34} = r_{56} = 1.54$ Å and $r_{23} = 1.32$ Å. The reaction can be imagined as occurring along either of two extreme reaction paths, the one involving the extension of the

TABLE I.

Reaction.	Bond Extension Energy Kg. Cals.		Repulsion Energy Kg. cals.	Energy of Crossing Point.	Heat of Reaction.
	Initial State.	Final State.			

Ring Formation.					
$2\text{CH}_2 : \text{CH}_2$	39.2 0	0 29.5	20.3 38.8	59.5 38.8	+ 33.8
$\text{CH}_2 : \text{CH} . \text{CH} : \text{CH}_2$ + $\text{CH}_2 : \text{CH}_2$	58.8 0	0 44.3	9.2 43.4	68.0 43.4	+ 28.4
$2\text{CH}_2 : \text{CH} . \text{CH} : \text{CH}_2$	78.5 0	0 59.0	4.6 48.4	83.1 48.4	+ 23.0

Biradical Formation.					
$2\text{CH}_2 : \text{CH}_2$	39.2 0	0 29.5	16.8 57.9	56.0 57.9	- 28.8
$\text{CH}_2 : \text{CH} . \text{CH} : \text{CH}_2$ + $\text{CH}_2 : \text{CH}_2$	39.2 0	0 29.5	14.7 48.4	53.9 48.4	- 18.8
$2\text{CH}_2 : \text{CH} . \text{CH} : \text{CH}_2$	39.2 0	0 29.5	12.0 38.3	51.2 38.3	- 8.8
$\text{CH}_2 . \text{CH} . \text{CH}_2' + \text{CH}_2 : \text{CH}_2$.	39.2 0	0 29.5	9.2 29.5	48.4 29.5	+ 1.5
$\text{CH}_2 . \text{CH} . \text{CH}_2'$ + $\text{CH}_2 : \text{CH} . \text{CH} : \text{CH}_2$	39.2 0	0 29.5	5.5 24.2	44.7 24.2	+ 11.5

C=C bonds in the initial state, the other a compression of the C—C bond distances in the final state. From the Morse functions for the C—C and C=C centres it is found that it requires less expenditure of energy to compress single bonds than to extend the double bonds. Not only does an extension of the molecular structure in the initial state involve an energy arising from the extension of isolated double bonds but it involves an extra expenditure of energy arising from a reduction in the energy of the mobile electrons. In general, therefore, the reaction path leading to the lowest value of the point of intersection of the two surfaces will be one in which the associated molecule is formed in a compressed state, that is, with the single bonds which have arisen from the opening up of double bonds at distances approximating to those in the initial state. Table I illustrates this point. It is seen from these figures that extension of the molecules in the initial state leads to a higher activation energy than does extension of the final state and hence in general the reaction will occur along a path involving the smallest extension of the initial state.

Another point to be noticed from this table is that the activation

TABLE II.

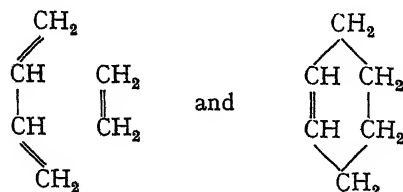
Reaction.	$h \times 10^3$ at 370°.	Activation Energy, Kg. Cals.
$2\text{CH}_2 : \text{CH}_2$	6.2	38.4
$2\text{CH}_2 : \text{CH} : \text{CH}_2$	2.0	38.0
$2\text{CH}_2 : \text{CH} : \text{CH} : \text{CH}_2$	1.1	38.0
$2 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{C} \parallel \text{CH}_2 \end{array}$	2.5	43.0

energies calculated by this method, that is, neglecting the resonance energy in the transition state, are of the magnitude of 40-50 kcals. These values are very much higher than those found experimentally for diene dimerisations. The value is, however, of the correct magnitude for the activation energy of dimerisation reactions not involving con-

jugated molecules but involving hydrocarbon centres which would exercise the same repulsion forces. Table II gives the results of the activation energies of bimolecular polymerisation reactions studied by Krauze, Nemtsof and Soskina.⁶

The Resonance Energy in the Transition State.

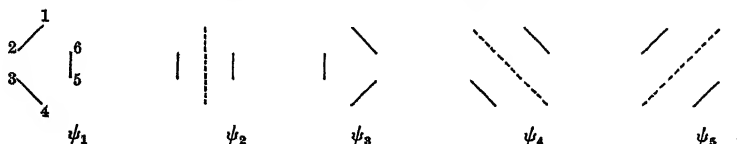
So far we have neglected resonance energy between the two bond assignments having approximately the same energy and the same configuration.* For example, in the case of a reaction between butadiene and ethylene the two bond assignments in the transition state are



⁶ Krauze, Nemtsof and Soskina, *Compt. Rend. U.R.S.S.*, 1934, **3**, 262.

* The influence of the resonance energy in the transition state of such reactions has already been discussed by Evans and Warhurst, *Trans. Far. Soc.*, 1938, **34**, 614.

In terms of the bond eigenfunction method the initial state can be defined in terms of the representations ψ_1 and ψ_2 .



whereas the final state will be given by ψ_3 . The transition state will be defined in terms of all five representations ψ_1 , ψ_2 , ψ_3 , ψ_4 and ψ_5 . These same forms can be expressed in terms of the conception of "mobile electrons." In the initial state the four π -electrons of the butadiene structure can be considered as moving in the periodic field of the carbon centres 1, 2, 3 and 4 and two π -electrons in the field of centres 5 and 6. The energy levels of the mobile electrons can be expressed in terms of the molecular orbital method as the roots of the determinant

$$| \int \bar{\phi}_i H \phi_j d\tau - E \int \bar{\phi}_i \phi_j d\tau | = 0,$$

where the ϕ 's are the eigenfunctions of the electrons in the field of the separate nuclei. If we assume in the initial state that the distances r_{12} , r_{23} , r_{34} , and r_{56} , are equal and that we can neglect the integrals $\int \bar{\phi}_i H \phi_j d\tau$ between non-adjacent centres, then the determinant giving the energy levels of the mobile electrons in the initial state is :

$$\begin{vmatrix} W & \beta & 0 & 0 & 0 & 0 \\ \beta & W & \beta & 0 & 0 & 0 \\ 0 & \beta & W & \beta & 0 & 0 \\ 0 & 0 & \beta & W & 0 & 0 \\ 0 & 0 & 0 & 0 & W & \beta \\ 0 & 0 & 0 & 0 & \beta & W \end{vmatrix} = 0, \quad \begin{array}{l} \text{where } W = Q - E = \int \bar{\phi}_i H \phi_i d\tau - E \int \bar{\phi}_i \phi_i d\tau \\ \text{and } \beta = \int \bar{\phi}_i H \phi_{i\pm 1} d\tau \text{ and } \int \bar{\phi}_i \phi_j d\tau = 0 \\ \text{when } i \neq j \end{array}$$

In the transition state, however, the freedom allowed to the mobile electrons has been increased by the introduction of the centres 1 to 6 which are now available to all six electrons. Thus the determinant becomes

$$\begin{vmatrix} W & \beta & 0 & 0 & 0 & \delta \\ \beta & W & \beta & 0 & 0 & 0 \\ 0 & \beta & W & \beta & 0 & 0 \\ 0 & 0 & \beta & W & \delta & 0 \\ 0 & 0 & 0 & \delta & W & \beta \\ \delta & 0 & 0 & 0 & \beta & W \end{vmatrix} = 0, \quad \text{where } \delta = \int \bar{\phi}_1 H \phi_6 d\tau = \int \bar{\phi}_6 H \phi_1 d\tau \text{ the exchange integral between the centres finally linked by } \sigma \text{ bonds.}$$

Very qualitatively we may say that whereas in the initial state the mobile electrons are those characteristic of an ethylene and a butadiene structure in the transition state they simulate the behaviour in a benzene structure. A similar argument can be applied to the reactions by the end on method attack where in the transition state the mobile electrons will tend to behave like those in hexatriene. The determinant for the energy of the mobile electrons in the transition state of this reaction will be

$$\begin{vmatrix} W & \beta & 0 & 0 & 0 & 0 \\ \beta & W & \beta & 0 & 0 & 0 \\ 0 & \beta & W & \beta & 0 & 0 \\ 0 & 0 & \beta & W & \delta & 0 \\ 0 & 0 & 0 & \delta & W & \beta \\ 0 & 0 & 0 & 0 & \beta & W \end{vmatrix} = 0.$$

This being the case there are qualitative rules which follow. The energy levels of the mobile electrons lie lower in cyclical structures than in straight chain compounds with the same number of centres available. The energy levels of the mobile electrons are lower the greater the number of available centres. These rules imply that the lowering of the activation energy due to the resonance effect will be greater in cyclisation reactions than in chain formation and that the resonance energy in the transition state will increase with the increasing degree of conjugation of the reacting molecules.

Table III shows the extra energy which is introduced in the transition state in these reactions. The value of δ can be obtained from the cross-section through the potential energy surface leading to the lowest energy of the crossing point. The value of δ is given by one half the exchange integral for the C—C bond at the distance of separation defined by the crossing point.

TABLE III.

Reaction.*	r_{C-C} at crossing point	δ .	δ/β .	E_R Kg. cals.	E_0 Kg. cals.	E_c Kg. cals.
$CH_2:CH:CH:CH_2$ + $CH_2:CH_2$	1.85	27.6	0.87	27.5	43.4	17
$2CH_2:CH:CH:CH_2$	1.72	31.4	1	23.5	48.4	25
$CH_2:CH:CH_2$ + $CH_2:CH_2$	1.54	32.3	1	20.1	29.5	9.4
$CH_2:CH:CH_2$ + $CH_2:CH:CH:CH_2$	1.72	31.4	1	21.7	24.2	2.5

E_R Resonance energy at the crossing point.

E_0 Activation energy of the crossing point.

E_c Corrected activation energy of transition state.

Application to Hydrocarbon Reactions.

The activation energies of diene association reactions are much lower than for reactions involving the same repulsion forces between carbon centres and similar heats of reaction. This is shown by comparing the results in Table IV with those in Table I.

TABLE IV.⁷

Reaction.	Activation energy Kg. cals.
2 butadiene . . .	25.3
2 isoprene . . .	28.9
2 dimethyl butadiene . . .	26.0
2 pentadiene . . .	25.3
2 cyclopentadiene . . .	16.7

In the light of the previous discussion we would suggest that this lowering of the activation energy arises from the increased mobility which the π electrons of such reactions possess in the transition state. Because of the conjugated structure of the reactants the formation

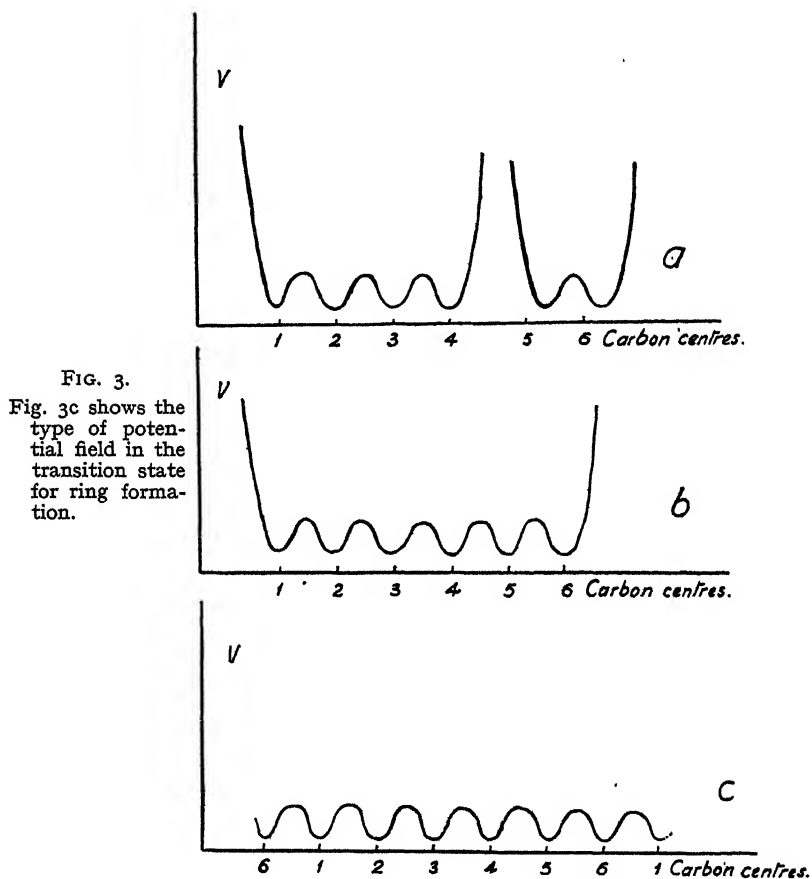
of the transition state increases the number of carbon centres which form the periodic field in which these electrons move. In Fig. 3a we represent diagrammatically the potential fields set up by the carbon

* Reactions 1 and 2 are ring dimerization and 3 and 4 chain formation.

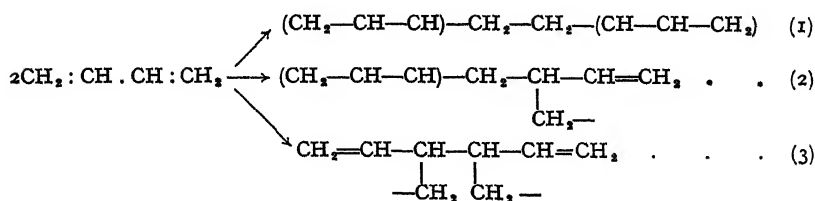
⁷ A very careful survey of the experimental work is given by Wasserman, *Trans. Far. Soc.*, 1938, **34**, 128.

centres of a butadiene and an ethylene molecule. The formation of the transition state is really the formation of a new carbon skeleton the potential field of which is shown in Fig. 3*b* and the increase in the length of the potential field lowers the energy levels of the mobile electrons and thus offsets the energy required to change the carbon skeleton from that of 3*a* to 3*b*.

In the chain building reactions the process is facilitated by the fact that the free radical formed is one in which the π electrons contribute very largely to the molecular energy thus tending to stabilise the radical

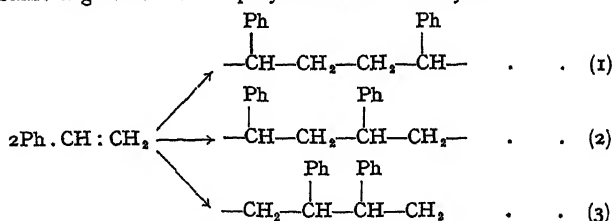


form. In a reaction in which several types of free radical are possible as a result of the primary step as for example:—



the following factors may determine the most likely step. (1) The production of the free radical form with the lowest energy for the mobile electrons. (2) The tendency to simulate the structures with the greatest paths and hence the lowest energy for the mobile electrons in the transition state.

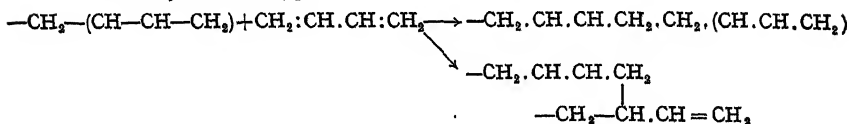
On this basis we would expect product 1 to be the most probable and applying the same argument to the polymerisation of styrene:



one would expect (1) to be the most probable product.

The subsequent steps in the polymerisation reaction will occur with much greater ease than the primary step, that is, in reactions in which free radicals are not artificially produced the primary step should be the slow one.

The subsequent steps which involve radical reactions will occur with small activation energies of the order of 5-10 Kcal., but here again the chain propagation will be determined by just those principles which determine the primary step. Thus in the chain propagation in the butadiene reaction the most probable one is that in which the terminal group is of the allyl radical type



Some preliminary work carried out by H. Walker⁸ on the recombination of free radicals formed by the action of sodium atoms on organic halides indicates that the greater the resonance energy in the free radicals the more efficient is the recombination as a bimolecular reaction. The points which we have discussed above might account for this observation. Firstly, the greater the resonance energy of the free radicals the smaller will be the heat of reaction. An extreme example of this is to be found in the heat of recombination of triphenyl methyl radicals. Secondly, the greater the mobility of the π -electrons in the transition state the greater will be the lowering of the activation energy. This will increase with the increasing resonance energy of the free radicals. Both these factors mean that less energy is contained in the newly formed link as the resonance energy of the radicals increases and hence the greater chance of bimolecular association reaction without the necessity for stabilisation by a third body.

Summary.

The activation energy of reactions involving conjugated molecules is discussed and it is suggested that the low activation energy for the dimerisation and polymerisation reactions is due to the large resonance energy in the transition state. The resonance energy is discussed in terms of the behaviour of the mobile electrons in the conjugated systems.

⁸H. Walker, M.Sc. Thesis, Manchester University.

CRITIQUE OF THE PAIR THEORY OF MESOMERISM.

BY E. H. LLOYD AND W. G. PENNEY.*

Received 7th February, 1939.

The theory of mesomerism, or resonance, in polyatomic molecules has been extensively developed. Detailed comparisons of observed and calculated energies of formation have been given, and the theory has been extended to cover other properties such as force constants and inter-nuclear distances. In spite of the excellent agreement which has been obtained, the validity of the theory has always been doubtful. The purpose of this paper is to improve the mode of presentation of the theory, and to discuss the type of calculation which may confidently be expected to lead to results of accuracy comparable with those of experiment. As we shall show, there are other types of calculation in which the theory is incapable of yielding such results, except by accident. For example, as we shall show, the energies of formation of molecules of mesomeric structure can be estimated simply from a knowledge of the energies of formation of molecules in which the mesomerism is negligible, but the error is about five times that of the experimental results.

Pauling and his collaborators¹ have developed a theory of mesomerism, and have applied it to systematise the thermochemical data on a large number of molecules. Their methods have apparently proved very successful. The reason for this, to a large extent, is that direct comparisons of large terms, or even of first order corrections to large terms, have been avoided. One would naturally expect that the thermochemical data on hydro-carbons could be successfully interpreted with three types of carbon-carbon bonds (apart from the triple bond, which, for the moment, we exclude). These might be called the single bond, the double bond, and the mesomeric bond, the latter being determined, let us say, from the energy of formation of benzene. By using the theory merely to evaluate departures of a mesomeric bond from the benzene bond, excellent agreement with experiment is assured. Such a procedure is, of course, perfectly legitimate, but the theory does seem a little elaborate for such a subsidiary task.

* Dr. Penney, when presenting this paper, added: The calculations given above can be extended. For example, the force field and vibration frequencies of the diacetylene molecule can be calculated, and the results agree well with experiment.

An indirect estimate of the heat of sublimation of carbon may also be made. Both by the orbital and pair methods the short wave-length limit of the fluorescent spectrum of benzene may be related to the difference ($w_b - w_s$). Since this difference involves the heat of sublimation of carbon, the heat can be estimated. We obtain 170 k.cal./mol., a value unlikely to be in error by more than 10 per cent. Herzberg, Herzfeld and Teller^{1a} have suggested 124 k.cal./mol., but we consider that their arguments are open to criticism. Full details will be published later.

¹ Pauling and Wheland, *J. Chem. Physics*, 1932, 1, 362; Pauling and Sherman, *ibid.*, 1933, 2, 606.

^{1a} *J. Physic. Chem.*, 1937, 41, 325.

Let us consider the line of argument used by Pauling and his collaborators. From inspection of the thermochemical data, bond energies $C-H$, $C-C$ and $C=C$ are chosen. The energy of formation of a molecule such as benzene is then estimated, assuming no mesomerism, from $6C-H+3C-C+3C=C$. The observed energy of formation is slightly greater than this, and the excess is called the "resonance energy." However, the fact that the benzene bond has a length that is neither that of the double bond nor of the single bond is ignored. The "resonance energy" is clearly a quantity of great practical importance. Notice the origin from which it is measured, namely, the molecule in a configuration where the bonds are rigorously single or double, all with their appropriate single and double bond lengths.

Pauling¹ now evaluates the energy of the most stable state of a ring of six similar, and similarly situated, monovalent atoms, in terms of a single parameter J . The energy of this state is $2.606 J$. If the bonds were alternately single and none, but all of the same length, the energy would be $1.5 J$. Thus the resonance energy is $1.106 J$. By equating this to 39.3 k.cal./mol., the observed resonance energy in benzene, the value $J = 35.5$ k.cal./mol. is obtained. However, in the theoretical problem the resonance energy is measured from the equilibrium position, and in the practical case, is measured from a non-equilibrium position.

Similar calculations on other molecules also give values for J , and they all agree very well with the benzene value. Such a result could not be predicted, nor even expected, from the theory in its present form; and the observed constancy of J does nothing to prove or disprove the theory. Nevertheless, as we shall show, the theory can be applied to predict the energies of formation of molecules of mesomeric structure, and the results are in very close agreement with those obtained by Pauling's method, using his value of J .

The Functions S and J .

According to the pair method, the energy of formation of a molecule may be partitioned into bonds. It is possible to obtain formulæ for the energy of the double bond and the benzene bond. Both of these are such that the carbon atoms have three bonds in a plane, making angles 120° with each other. The theory, subject to its usual limitations and approximations, gives

$$W_d(r) = S(r) + \frac{1}{2}J(r) \quad . \quad . \quad . \quad (1)$$

$$W_b(r) = S(r) - 0.066J(r) \quad . \quad . \quad . \quad (2)$$

where the functions $S(r)$ and $J(r)$ are the same in both cases. The function $J(r)$ is an exchange integral between two p_h electrons, distance r apart, and $S(r)$ is the sum of a number of exchange and Coulomb integrals, taken at distance r . The first equation is obtained as follows. The energy of the coupled p_h electrons of the double bond is J ; subtracting $\frac{1}{2}J$ for the interaction of the p_h electrons in the localised trigonal bonds gives the energy as $\frac{1}{2}J$. To this must be added the Coulomb energy, and the energy of the other bond. Together, these give S .

The form of the second equation is obtained from the solution $W = 2.606 J$, found by Pauling and Wheland¹ for the energy of a ring of six monovalent atoms. The energy per atom is $0.434 J$; subtracting $\frac{1}{2}J$ for the interaction of the p_h electrons in the plane of the ring gives the energy as $-0.066 J$. To this must be added the Coulomb energy and the energy of the localised bonds, *i.e.*, the function S .

Solving (1) and (2) for S and J , we find

$$S = 0.117 W_d + 0.873 W_b \quad (3)$$

$$J = 1.767 (W_d - W_b) \quad (4)$$

Curves for W_d and W_b may be obtained from the experimental data. Hence curves for S and J may be constructed. To construct the curves for the two W 's, we make use of the Morse function

$$W(r) = W[2e^{-a(r-r_0)} - e^{-2a(r-r_0)}],$$

where r_0 is the equilibrium distance for the bond, W is the energy of formation of the bond, and the parameter a is given by the relation

$$k = 2Wa^2$$

k being the force constant.

The relevant experimental material is given in Table I.

The units are k.cal./mol. for W , Ångströms for r , 10^5 dynes per cm. for k , and reciprocal Ångströms for a . The bond energies are those given by Pauling and Sherman,¹ the force constant for the double bond that given by Sutherland and Dennison,² and that for the benzene bond has been obtained from the two vibrations of benzene in which both carbon and hydrogen atoms remain at the corners of regular hexagons (vibrations A_{1g}) in the notation of Ingold and collaborators,³ together with the assumption of a valence force field.

Fig. 1 shows the variations of the functions $S(r)$ and $J(r)$ with r .

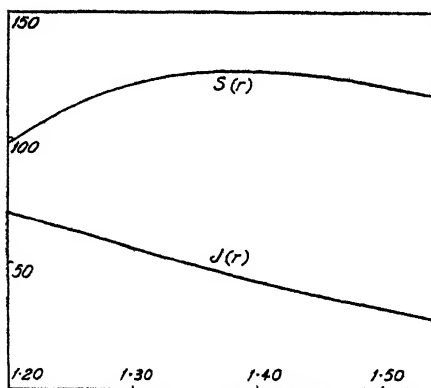


FIG. 1.—The Fig. shows the variation with r of the functions J and S . The units of r are Ångströms, and of S and J are k.cal./mol.

The value of $J(r)$ at the benzene distance is 43 k.cal./mol. or 1.85 e.v. Sklar⁴ assumes 1.92 e.v. in order to explain the fluorescent spectrum of benzene and other molecules.

The Single and the Triple Bonds.

Formulae similar to (1) and (2) may be given for the single and the triple bonds. However, for the single bond the valency bonds of the carbon atom are based on tetrahedral wave functions, and for the triple bond, are based on linear wave functions. Hence in these cases the functions $S(r)$ will be slightly different from that of (1) and (2). Similar difference would also

² Sutherland and Dennison, *Proc. Roy. Soc., A*, 1935, 148, 250.

³ Ingold and collaborators, *J. Chem. Soc.*, 1937, 974.

⁴ Sklar, *J. Chem. Physics*, 1937, 5, 669.

be expected in the C—H bonds, but according to the experimental data, the C—H bond is so near constancy that variations in it cannot be detected. Let us make the assumption that there is a similar constancy in the function $S(r)$. Then the energies of the single and triple bonds are

$$W_s = S(r) - J(r) \quad . \quad . \quad . \quad . \quad (5)$$

$$W_t = S(r) + 2J(r) \quad . \quad . \quad . \quad . \quad (6)$$

Substituting $S(r)$ and $J(r)$ from (3) and (4) and minimising with respect to r gives the energies and lengths of the bonds, and by expanding about

TABLE II.

	Single Bond.		Triple Bond.	
	Calculated.	Observed.	Calculated.	Observed.
W	88.7	84	240	199
r_0	1.52	1.54	1.22	1.20
k	4.95	5.0	13.4	15.0

the minimal positions the force constants are obtained. The results are given in Table II, and for comparison the experimental results are also given.

From an inspection of Table II it is seen that the calculated lengths of the links are about right,

but that the error in the energies is considerable. The functions $S(r)$ can, of course, be adjusted to make the theory agree with experiment, but the variations which must be introduced are of the opposite sign to those that we would have expected.

From equations (1) and (5) it is also possible to solve for W_b , and hence to find the energy, length and force constant of the benzene bond. The energy is 120.2, the length 1.408 and the force constant 8.04. Thus, the energy of a mesomeric link, when calculated from the properties of single and double bonds, is in error by about 4 k.cal./mol. This is roughly five times the experimental uncertainty.

The Butadiene Molecule.

We have selected this molecule for discussion because the links in this case offer a contrast with those of benzene. Thus the two outer links are very close to double bonds, and the central link is intermediate to the single bond and the benzene bond. Denote quantities relating to the outer two carbon-carbon bonds by a suffix 2, and to the central carbon-carbon link by a suffix 1. The resonance problem is that of four electrons, the solution of which has been given many times (see, for example, Van Vleck and Sherman).⁵ Adding $6(\text{C—H}) + 2S_2 + S_1 - J_2 - \frac{1}{2}J_1$ for the localised bonds, where C—H has the value 99 k.cal./mol., we get the energy of formation of the molecule from atoms as

$$W = 6(\text{C—H}) + 2S_2 + S_1 - J_2 - \frac{1}{2}J_1 + (J_1^2 + 4J_2^2 - 2J_1J_2)^{\frac{1}{2}} \quad (7)$$

Minimising this with respect to r_1 and r_2 , we find that

$$r_1 = 1.44, r_2 = 1.34, J_1 = 31.7, J_2 = 50.0, W = 987.$$

According to Pauling's argument

$$W = 6(\text{C—H}) + 2(\text{C}=\text{C}) + (\text{C}=\text{C}) + (\sqrt{3} - 1.5)J.$$

⁵ Van Vleck and Sherman, *Rev. Mod. Physics*, 1935, 7, 167.

Substituting for the bond energies, and taking $J = 36$, we find $W = 987$, in exact agreement with the value above. Thus, although the distances r_1 and r_2 are appreciably different, and the two exchange integrals J_1 and J_2 are widely different, the net result agrees very well with that obtained from the theory based on bonds of equal length and a value of J chosen to fit the resonance energy in benzene. Similar agreement may be expected for other molecules since the variations between the different bonds for these will be less than the variation in butadiene.

The Benzene Molecule.

One of the achievements of the theory of mesomerism is generally considered to be that it proves that all linkages between neighbouring carbon atoms in the benzene ring are similar. What has really been done, however, is to show by quantum mechanics that if the C—C distances are the same, the linkages are equivalent. Arguments of symmetry of a much more general type, independent of quantum mechanics, would lead to the same conclusion.

Lennard-Jones⁶ has attempted to show by approximations based on molecular orbitals, that the regular hexagon structure is more stable than a structure in which alternate links are longer and shorter respectively than their average. His demonstration is satisfactory up to a point, but it is subject to the following disadvantage. The orbital method does not directly predict the additivity property of bond energies. Thus, for example, it is not possible by the orbital method to obtain a closed formula for the energy of formation of benzene, in which certain terms will represent the C—H energy and will be the same per bond as those in ethylene. Lennard-Jones avoided this difficulty by concentrating on the mobile electrons, and representing the rest by a potential energy, controlled by an empirical single force constant.

According to the pair method, as we have already explained, exact formulæ, *viz.*, (1) and (2), can be obtained for the energy of the double and the benzene bond. We shall now make use of the functions S and J so determined, to prove that the theory is self-consistent in that it gives the regular structure as being the most stable. At the same time we shall show that the molecule is easily distorted in a certain way, and shall then estimate one of the fundamental vibration frequencies.

Suppose that the links round the hexagon are alternately longer and shorter than their average, the former being denoted by a suffix 1 and the latter by a suffix 2. The resonance problem reduces to a cubic, and by a method explained by Wheland,⁷ is easily obtained in the form

$$E^3 + E^2(J_1 + J_2) - 3E(3J_1^2 + 3J_2^2 - 2J_1J_2) - 9(J_1^2 - J_2^2)(J_1 - J_2) = 0. \quad (8)$$

Let E_{12} be the energy of the lowest state, obtained by solving this equation. The energy of formation of the molecule is

$$W = 6(\text{C—H}) + 3S_1 + 3S_2 + E_{12} - 3(J_1 + J_2)/2.$$

Minimising this with respect to r_1 and r_2 , it is found that $r_1 = r_2$; and hence the regular structure is the most stable.

Suppose that the ring is slightly distorted from the symmetrical position in such a way that all the 120° angles are preserved (distortion $B_{2u}(C)$ in the notation of Ingold and collaborators⁸). Write

$$r_1 = r_0 + \epsilon, \quad r_2 = r_0 - \epsilon.$$

⁶ Lennard-Jones, *Proc. Roy. Soc., A*, 1936, 158, 280.

⁷ Wheland, *J. Chem. Physics*, 1935, 3, 230.

Substitute in the expression for W and hence find a force constant k_s such that for displacements ϵ

$$\delta V = 3k_s \epsilon^2.$$

Then in the vibration $B_{2u}(C)$

$$\begin{aligned} \delta T &= (m + M)\dot{\epsilon}^2 \\ 4\pi^2\nu^2 &= 3k_s/(m + M), \end{aligned}$$

where m is the mass of a hydrogen atom, and M is the mass of a carbon atom. We find $k_s = 1.55 \times 10^5$ dynes per cm., and $\nu = 780$ cm.⁻¹.

Let us now estimate the difference in energy of the benzene molecule in its most stable state and in a state where alternate links round the ring have single and double bond lengths respectively. Substituting the appropriate values for J_1 , J_2 , S_1 and S_2 , and solving (8) for E_{12} , we find that the regular configuration is 10 k.cal./mol. more stable than the other position. Thus the resonance energy in the position where the bonds have alternately single and double bond lengths is as great as 20 k.cal./mol. The forces holding the molecule in the symmetrical position are comparatively weak.

The Allene Molecule.

The allene molecule in its equilibrium position has negligible mesomerism, but in its planar form the mesomerism is considerable.

The energy of the stable form is

$$4(C - H) + 2S_d + J_d$$

where the suffix d means evaluated at the double bond distance.

The molecule in the perpendicular form has a resonating system of three electrons, and the energy is

$$4(C - H) + 2S_a.$$

The difference in energy of plane and perpendicular allene is thus J . This is to be compared with a difference $3J/2$ in ethylene.⁸ According to the present argument therefore, the twisting frequency in allene should be $(2/3)^{1/2}$ that in ethylene. Linnett and Avery⁹ have suggested that the two twisting frequencies should be in the ratio $1 : \sqrt{2}$.

The Diacetylene Molecule.

The diacetylene molecule $HC \equiv C - C \equiv CH$ is presumably linear. According to the accepted ideas on mesomerism, the central bond should be considerably stronger than an ordinary single bond, and as strong, perhaps, as a double bond. This is not confirmed by deductions of the force field of the molecule, derived from the fundamental frequencies of the molecule. According to Timm and Mecke,¹⁰ the force constant of the central link is 4.5, and according to Wu¹¹ it is 3, the units in each case being 10^5 dynes per cm. Possibly the fundamentals have been wrongly assigned.

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⁸ Penney, *Proc. Physic. Soc.*, 1934, 46, 333.

⁹ Linnett and Avery, *J. Chem. Physics*, 1938, 6, 686.

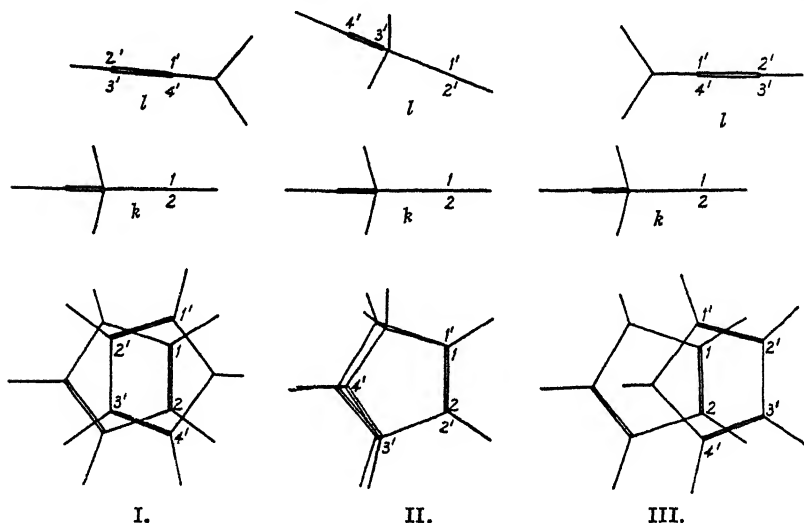
¹⁰ Timm and Mecke, *Z. Physik*, 1935, 94, 1.

¹¹ Wu, *Chinese J. Physics*, 1936, 2, 128.

GENERAL DISCUSSION.*

Dr. A. Wassermann (London) said: The course of certain diene associations is characterised by two facts: Formation of the 1:4-addition product and not of the 1:2-addition product, and steric selectivity. A typical example is the homogenous bimolecular association of gaseous cyclopentadiene. Under the conditions of the kinetic measurements¹ only the endoform² of the 1:4-addition product is formed; 1:2-addition or exo 1:4-addition does not take place.

Mutual orientations of the cyclopentadiene molecules, *l* and *k*, in the three transition states which are suitable for endo 1:4-addition, 1:2-addition and exo 1:4-addition are schematically represented below.³



Orientation I.

Suitable for the formation of endo-Dicyclopentadiene (endo 1:4-addition).

Orientation II.

Suitable for the formation of an hypothetical 1:2-addition product (1:2-addition).

Orientation III.

Suitable for the formation of exo-Dicyclopentadiene (exo 1:4 addition).

It is probable that the observed course of the dimerisation is due to the fact that the potential energy of the molecules in orientation I is smaller than that of the reactants in orientation II or III and it is of interest that the theoretical considerations of Evans⁴ provide a plausible explanation for the energy difference between I and II.

In case I and III, however, the resonance energy should be similar and I suggest, therefore, that the stabilisation of the transition state I

* On the three preceding papers.

¹ See *J. Chem. Soc.*, 1939, 362.

² For endo-exo-isomerism of dicyclopentadiene, see Alder and Stein, *Annalen*, 1932, 496, 232; 1933, 504, 238; *Angew. Chem.*, 1934, 47, 837.

³ For similar drawings in the case of other diene syntheses, cf. *J. Chem. Soc.*, 1935, 828, 1511; Alder, *Angew. Chem.*, 1937, 50, 510.

⁴ Cf. also Evans and Warhurst, *Trans. Faraday Soc.*, 1938, 34, 614.

is not only due to the resonance energy but also to the van der Waal's attraction energy (dispersion effect). The data in table I show that on the whole the closest packing of the various atoms occurs in orientation I, in which the van der Waal's energy is assumed to be larger than in either II or III. The figures relate to an atomic distance of 2.33 Å, between the atoms 1 and 1', *cf.* figures, but similar packing ratios are obtained for other molecular separations.

TABLE I.—DISTANCE BETWEEN CARBON AND HYDROGEN ATOMS IN DIFFERENT TRANSITION STATES OF THE CYCLO PENTADIENE ASSOCIATION.

		Transition State suitable for		
		Endo 1:4-addition. (Orientation I.)	1:2-addition. (Orientation II.)	Exo 1:4-addition. (Orientation III.)
Number of carbon atoms of (<i>l</i>) which are at a distance not more than α Å from the carbon atoms of (<i>k</i>)	α			
	2.3	2	2	2
	2.4	4	2	2
Number of carbon atoms of (<i>l</i>) which are at a distance not more than β Å from the hydrogen atoms of (<i>k</i>)	β			
	1.8	1	0	0
	2.5	3	1	5
Number of hydrogen atoms of (<i>l</i>) which are at a distance not more than γ Å from the carbon atoms of (<i>k</i>)	γ			
	2.3	1	3	1
	2.4	2	3	1
Number of hydrogen atoms of (<i>l</i>) which are at a distance not more than θ Å from the hydrogen atoms of (<i>k</i>)	θ			
	1.6	1	1	0
	2.0	2	3	2
	2.4	3	3	2
	2.6	5	3	4

The dispersion effect is inversely proportional to the sixth power of the distance between the various bonds⁵ and, therefore, the assumption that the van der Waal's energy in I is larger than in II or III is justified.

The potential energy of all three transition states is the sum of the attraction and the repulsion energy. If all those bonds which contribute to the attraction also contributed to the repulsion then the most closely packed transition state I would probably be less stable than II or III. The actually observed course of the dimerisation shows, however, that this is improbable. As a first approximation it seems justified to assume that the repulsion energy between the molecules in the three transition states is similar because only a limited number of bonds, *e.g.*, those between the reacting centres of the cyclo pentadiene molecules (atoms 1, 2, 1'4' or 1'2') contribute to the repulsion. This assumption cannot be proved but is not unreasonable since it is known that the repulsion energy is inversely proportional to a higher power of the distance than the attraction energy.⁶

⁵ London, *Z. Physik*, 1930, 63, 243; *Z. physikal. Chem.*, B, 1930, 11, 222; *cf.* also Wassermann, *J. Chem. Soc.*, 1936, 432; *Trans. Faraday Soc.*, 1938, 34, 28.

⁶ The treatment given by Evans is also characterised by the assumption that only a limited number of the atoms of the reacting molecules contribute to the repulsion energy.

In attempting to explain the course of other diene associations, *e.g.*, the addition of cyclopentadiene to benzoquinone, it has to be taken into account that the attraction energy is the sum of the dispersion effect and the dipole induction energy; the other considerations are similar to those given above.

Prof. G. B. Kistiakowsky (*Cambridge, Mass.*) (*communicated*): The mechanism of diene polymerisation through the intermediate formation of a bi-radical, discussed in the papers of Lennard-Jones and Coulson and of Evans, has been already proposed by Harkness, Kistiakowsky and Mears who considered the resonance of the bi-radical and the energetics of its formation.⁷ Since then Mr. W. W. Ransom and myself have remeasured the rate of dimerisation of butadiene over a wide temperature range and have then applied the statistical theory of reaction rates (Eyring) to this problem. Using the resonating bi-radical as the model of the activated complex and applying to it the same approximate methods of calculation of its thermodynamic functions, as have been used with success by others for ordinary hydrocarbon molecules, we have calculated the theoretical frequency factor of the dimerisation rate as 1.8×10^{10} c.c. mole⁻¹ sec.⁻¹, while the experimental value is 0.9×10^{10} . Similar calculations with a cyclic activated complex, having the structure of the final product, the Δ^3 -vinylcyclohexene, give a frequency factor of the order of 10^6 and show that the bi-radical mechanism is decidedly more probable. The details of the new results will be published shortly in *J. Chem. Physics*.

Dr. A. R. Ubbelohde (*London*) (*Communicated*):

Some Thermal Properties of Hydrocarbons.

The object of this note is to point out that the modes of vibration of various types of hydrocarbon molecules may be of considerable importance in elucidating their physical or chemical behaviour. It is convenient to treat normal paraffins as representative hydrocarbons for discussion; modifications for the presence of side chains, of unsaturation, or of aromatic or aliphatic rings are readily introduced when necessary.

1. The Structure of Polymethylene Liquids.—So far as is known, the latent heat of fusion of a paraffin increases continuously with the number of CH_2 groups, and might be as much as 500,000 cal./mole for $\text{C}_{1000}\text{H}_{2002}$. In spite of these enormous heats of fusion, it is a striking fact that there is a convergence temperature above which the substance is liquid, however much the size of the molecule is increased. For paraffins this temperature has been estimated⁸ to be about 400° K. It is obviously important in such problems as the Fischer-Tropsch synthesis, or the hydrogenation of coal, to discuss in what way liquids which can have enormous polymethylene molecules may be expected to differ from liquids whose properties are more familiar. The fact that for these molecules such high latent heats of fusion are accompanied by comparatively low melting-points has been explained⁸ by the assumption that each methylene group melts practically independently. This behaviour is almost certainly due to the possibility of torsional oscillations in polymethylene chains. When the chains are stiffened by unsaturation, especially in conjugated systems, such as the polyenes, higher melting-points may be expected as the latent heat of fusion rises.⁹ Similarly in polynuclear aromatic hydrocarbons the molecules are much more rigid, and the melting points for a similar number of carbon atoms are much higher.

In view of the fact that polymethylene molecules can exist in the liquid state at abnormally low temperatures, it is not surprising that X-ray

⁷ *J. Chem. Physics*, 1937, **5**, 682.

⁸ A. King and W. Garner, *J.C.S.*, 1936, 1368.

⁹ Cf. J. W. Oldham and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1939, **35**, 328.

investigations show the molecules to be roughly parallel.¹⁰ For longer chains and near the melting point this behaviour may be expected to be even more pronounced, and the packing structure in the liquids should lead to entropies of vaporisation above the normal value given by Trouton's constant. The *free volume*¹¹ will be abnormally small, and the solvent power for molecules which do not fit easily into the liquid "structure" must likewise be small. Data for the calculation of the entropy of vaporisation of the liquid are not abundant, since although formulae for the boiling-point of homologues have been frequently suggested,¹² the latent heats may be expected to have a large temperature coefficient.¹³ Nevertheless, rough calculations can be made from the data of Francis and Wood,¹⁴ and Ubbelohde.¹⁰ These show that entropies of vaporisation even when calculated according to the method of Hildebrand¹⁵ are abnormal for polymethylene liquids.

[In view of the limited experimental evidence it should be added, however, that theoretical considerations of Berger¹⁶ would lead to normal values of Trouton's constant, if they are applicable, since both the boiling-point and the heat of vaporisation increase proportionately to the square root of the molecular weight.]

In view of the "structure" of polymethylene liquids it is easy to understand that branch chain molecules with the same number of carbon atoms are more volatile, since the inner groups are shielded from the van der Waals' attractions of neighbouring molecules.

2. Adsorption of Polymethylene Molecules on a Catalyst.—Broda and Mark¹⁷ calculate that the adsorption of a molecule increases rapidly with chain length, but have apparently only considered the case where the molecule makes an "anchored" contact at every point of the chain. If their conclusions were applicable to the Fischer-Tropsch synthesis long hydrocarbon chains would be strong poisons for the catalyst. Qualitative considerations suggest, however, that the increased freedom of torsional oscillations of a polymethylene molecule compared with a polyene molecule must lead to relatively smaller adsorption for fully reduced chains. Experimental information on the extent to which homologous molecules are adsorbed would be of considerable interest.

3. Reactivity of Different Hydrogen Atoms in a Hydrocarbon.—The preferential attack of any particular hydrogen atom in a hydrocarbon reaction might be due either to the magnitude of the free energy change¹⁸ or to differences in the activation energy and steric factor at various parts of the molecule. Tertiary hydrogen atoms might be expected to be the most reactive in hydrocarbon chemistry, since they are less firmly bound owing to the repulsion of the neighbouring groups.¹⁹ It has even been suggested²⁰ that some kind of weak bond is formed between adjacent polyvalent atoms, in order to explain the inner rotation phenomena of carbon chains.

The fact that "end attack" is nevertheless frequently observed in the chemistry of hydrocarbons might of course be explained by the fact that in the approach of a second molecule much less repulsion is experienced in this way. At the same time, in view of the comparatively high frequency of the fundamental C—C vibration, the mechanism of the *supply*

¹⁰ Refs. in Ubbelohde, *Trans. Faraday Soc.*, 1938, **34**, 282.

¹¹ Cf. J. A. V. Butler, *Ann. Rep., Chem. Soc.*, 1937, **34**, 81.

¹² Boggia-Lera, *Gazz. Chim. Ital.*, 1899, **29**, 1, 441; A. W. Aten, *J. Chem. Physics*, 1937, **5**, 260; J. H. Merckel, *P.K.A.W. Amst.*, 1937, **40**, 164.

¹³ Ubbelohde², p. 291, for an estimate.

¹⁴ *J.C.S.*, 1926, 1420.

¹⁵ *J.A.C.S.*, 1915, **37**, 970.

¹⁶ *Rec. Trav. Chim.*, 1936, **56**, 599.

¹⁷ *Z. physik. Chem.*, 1937, **180**, 392.

¹⁸ Cf. Taylor and Turkevich, *this vol.*, p. 921.

¹⁹ Cf. refs. in Ubbelohde, *Proc. Roy. Soc., A*, 1935, **152**, 361.

²⁰ G. Kistiakowsky, J. Lacher, and W. Ransom, *J. Chem. Physics*, 1938, **6**, 900.

of activation energy to different parts of the molecule must be important, and involves a discussion of the modes of vibration of the molecule. A simplified discussion has been given previously¹⁹ but much more experimental data is now available.²¹

²¹ Cf. also L. S. Kassel, *J. Chem. Physics*, 1935, 3, 326.

THE APPLICATION OF THE NITRIC OXIDE METHOD TO THE INVESTIGATION OF REACTION CHAINS IN THE DECOMPOSITION OF HYDROCARBONS.

BY L. A. K. STAVELEY AND C. N. HINSHELWOOD.

Received 25th January, 1939.

Some reactions are considerably retarded by the presence of very small quantities of nitric oxide in a way which indicates the existence of chains, and which, with very reasonable assumptions, gives information about the proportion of molecules reacting by the chain mechanism. The general result of investigations carried out by this method¹ is that some, though by no means all organic decompositions, in the gaseous state, involve chains, and that the average length of the chains is often quite short. This is not because of the shortness of individual chains but because most of the primary processes are direct rearrangements to saturated molecules. Energy considerations show that the production of free radicals is improbable, but that once produced they should give rise to long chains. If the activation energy of an alternative rearrangement process is small enough it will predominate: the proportion of chain reaction depends upon the relative magnitude of various activation energies. Several hydrocarbon decompositions have been studied in this way.² The significance of the results depends upon the validity of the particular interpretation we give them: this must first be considered.

The important factors are quantitative ones: 1 mm. of nitric oxide may reduce to a fraction of its original value the rate of reaction of several hundred times its own amount of the organic substance. The nitric oxide is gradually used up, but usually only slowly. For example: 2 mm. nitric oxide will last out the decomposition of 400 mm. diethyl ether which in the meantime is reacting at about one-third the normal rate. Sometimes the nitric oxide may be used up before the decomposition is over. This occurs with dimethyl ether, but even here some twenty molecules of the ether decompose at a greatly reduced rate before the one of nitric oxide is consumed and the rate rises rather abruptly to normal again. The first detectable products are oxidation products of the organic compound and reduction products of nitric oxide, such as

¹ Staveley and Hinshelwood, *Nature*, 1936, 137, 29; *Proc. Roy. Soc., A*, 1936, 154, 335; *J.C.S.*, 1936, 812; *Proc. Roy. Soc., A*, 1937, 159, 192; *J.C.S.*, 1937, 1568; Hinshelwood and Staveley, *J.C.S.*, 1936, 818; Mitchell and Hinshelwood, *Proc. Roy. Soc., A*, 1937, 159, 32.

² Staveley, *Proc. Roy. Soc., A*, 1937, 162, 557; Hobbs and Hinshelwood, *Proc. Roy. Soc., A*, 1938, 167, 439, 447; Hobbs, *ibid.*, 456.

ammonia,³ but these must be the result of a series of changes, probably starting with the direct union of an organic radical and the nitric oxide, which, electronically, is itself a free radical.

Since one molecule of nitric oxide by reacting with something in the system can stop the reaction of several hundred molecules of an organic compound, the something which it removes in its own reaction must normally have been responsible for the decomposition of a large number of molecules. This is what is known as breaking a chain.* By this criterion the decomposition of hydrocarbons at 500°-600° proves to involve the participation of chain reactions to some extent.

The next important fact is that the nitric oxide reduces the reaction rate, not to zero but to a quite definite limit. The rate does not in general simply fall to a minimum and then rise again, but remains steady at the limit over a relatively wide range. With ether, for example, it falls rapidly over the range 0.2 mm. and then remains nearly constant for about ten times this range. Later the rate rises again, large amounts of nitric oxide showing a positive catalytic effect as well as appreciable

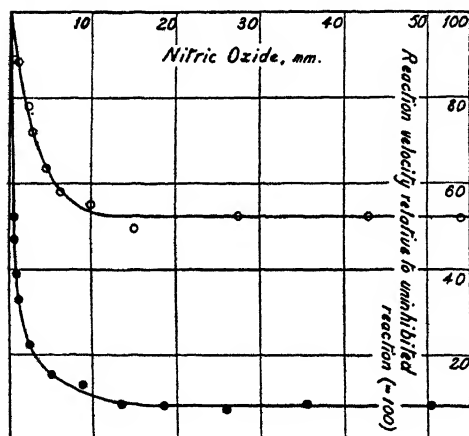


FIG. 1.— Showing how the reaction velocity reaches a steady limiting value as the nitric oxide pressure increases. The upper curve (open circles) is for 100 mm. of hexane at 530° C., the lower (full circles) for 150 mm. of ethane at 620° C.

reaction with the ether. It has been suggested that this limiting rate is not of quantitative significance, and that it is simply a minimum, representing a state where nitric oxide starts as many chains as it stops. This view is difficult to reconcile with several facts. (1) The extreme definiteness of the limit in many examples. In Fig. 1 the limit does not in the least resemble a minimum of the kind suggested. (2) The reduction of the quantum yield in the photochemical decomposition of acetaldehyde from several hundred to nearly unity by the addition of nitric oxide. (3) The admission of minute amounts of nitric oxide into a stream of ether issuing from a furnace at 800° C. inhibits the removal of tellurium mirrors. (4) The positive catalytic effect which appears at higher pressures of nitric oxide is a phenomenon on a different scale from that of the inhibition and could hardly be supposed to compete on equal terms with it.

³ Thompson and Meissner, *Nature*, 1937, 139, 1018.

* This somewhat didactic statement may seem superfluous, but is useful in guarding against the misunderstanding that the validity of the nitric oxide method is affected by the complex reactions which can occur when nitric oxide and hydrocarbons are heated together in more or less equivalent proportions.

At the present time there seems to be no evidence for doubting that the nitric oxide suppresses all the chains. Thus, by a reasonable hypothesis, the ratio of the original to the limiting rate may be taken to give information about the proportion of chain reaction present. Moreover, the radicals which certain compounds would give if they reacted by a chain mechanism are similar to those from others known to be sensitive to nitric oxide, yet the decomposition of these former compounds is not inhibited by nitric oxide. One may therefore reasonably conclude that no chains are involved.

Judged by this criterion the hydrocarbons decompose by chain mechanisms, but the mean chain lengths are not in general great. The mean chain length is defined as the ratio of the rates of the uninhibited and fully inhibited reactions. The values found for hydrocarbons are as follows:

Methane	4.7 at 850° C. and 100 mm. pressure.		
Ethane	17.8 at 600° C.	"	"
Propane	7.5 at 550° C.	"	"
Hexane	1.9 at 530° C.	"	"

The activation energy of the fully inhibited reaction must relate directly to the residual primary processes, if all the chains are completely suppressed. This activation energy is always less than the energy required to break the carbon-carbon bond, the difference (about 20,000 cal.) being most marked with the ethers and aldehydes. The majority of the primary processes must therefore be direct rearrangements into normal molecules and only a small fraction can involve the production of radicals. Hence the average absolute length of the chains set up by these few radicals must be fairly large. Until we know precisely what fraction of primary processes produces radicals, we cannot derive the absolute length of the chains from the mean chain length, but this latter quantity does, in a sense, measure the extent to which the normal uninhibited decomposition proceeds by a chain mechanism.

A few millimetres of nitric oxide can usually last out the decomposition of several hundred millimetres of the hydrocarbon, ether, or aldehyde, and this supports the conclusion that the absolute chain length is large. If it were in fact equal to the mean chain length, that is, if every primary process were the breaking of the molecule into two radicals, then the nitric oxide should rapidly disappear from the system. (Photochemical experiments at lower temperatures have shown that one molecule of the inhibitor is removed for each chain broken). Dimethyl ether, however, is exceptional in that the nitric oxide is fairly rapidly used up at a rate which sets a lower limit of about 400 to the absolute length of the chains.

If, on the other hand, the chains in these thermal decomposition reactions were sufficiently long for the wall of the reaction vessel to play as important a part in breaking them as it does in the hydrogen-oxygen reaction, then packing the bulb should retard the decomposition considerably. Actually, a ten-fold increase in the surface/volume ratio seldom produces more than a 10-20 per cent. drop in reaction velocity. The effect is somewhat larger with hexane, and it may be that the absolute chain length here is greater than in the other reactions so far studied.

In previous papers we have suggested values (all of the order 10,000 cal.) for the activation energy of the reaction between the radical and the hydrocarbon. These estimates were based on the assumption that at the concentration of nitric oxide required to produce half the maximum

inhibition, the chain propagating radical has an equal chance of being removed from the system by combining with a molecule of nitric oxide or of continuing the chain by reacting with the hydrocarbon.* A reconsideration of this problem has shown that this condition is not fulfilled until much more nitric oxide has been added than is required to inhibit the reaction to half the maximum possible degree. If, as was formerly assumed, every collision between a nitric oxide molecule and a radical leads to the removal of the latter, then collisions between radicals and hydrocarbon molecules more often give rise to reaction than we have hitherto supposed, that is, the activation energies of these reactions are less than the 10,000 cal. or so previously proposed for them. But an entirely independent method gives values of a similar magnitude for the reaction between aldehyde molecules and photochemically produced radicals, and it may be that their reaction with hydrocarbon molecules does, in fact, have about the same activation energy, but that not every collision of a radical with nitric oxide leads to its removal from the system.

In the absence of nitric oxide, chains may end either by a simple binary recombination of two radicals, or a third molecule may be required to absorb the energy evolved. The smaller the chain carrying particles, the more likely are they to require a triple collision. All the hydrocarbons so far studied show a decrease in the mean chain length as the pressure increases, which can only be accounted for if it is assumed that the recombination of the radicals is predominantly a ternary process. The question can be attacked in another way. In the presence of nitric oxide the inhibitor competes with the normal method of chain-breaking. Whether or not the hydrocarbon molecules take part in it should therefore be revealed by the form of the curve obtained by plotting reaction velocity against nitric oxide pressure. The curves for the decomposition of ethane at various pressures are shown in Fig. 2, where the quantity $(\rho - \rho_{\infty})/(\rho_0 - \rho_{\infty})$ is plotted against the nitric oxide pressure. ρ is the measured rate for a given nitric oxide concentration, and ρ_0 and ρ_{∞} are respectively the rates of the uninhibited and fully inhibited reaction. $(\rho - \rho_{\infty})/(\rho_0 - \rho_{\infty})$ is therefore independent of the contributions which the non-chain rearrangement processes and any accompanying surface reaction make to the total rate. Equations can be derived to fit these curves if the rate of the normal chain-ending process is assumed proportional to the square of the radical concentration and to a power of the ethane pressure of about 0.6 or 0.7. This result is interpreted to mean that either there are two independent chain-ending mechanisms, one a binary and the other a ternary process, or else a single process whose order depends on the pressure. The first possibility implies that binary collisions predominate at lower pressures, and ternary at higher pressures. If the second alternative holds, then it can easily be shown that the mean life of the activated association product of the two radicals must be at least of the order of magnitude of the time between two collisions with ethane. On chemical grounds it seems almost certain that both hydrogen and ethyl radicals participate in the chain cycle, and so there are three possible chain-breaking reactions. Two hydrogen atoms could combine in a triple collision with an ethane molecule, or a hydrogen atom and an ethyl radical in either a binary or a ternary process, while two ethyl

* With the ethers it appears that the velocity of propagation of the chains depends on the rate of decomposition of a large radical. In calculating the mean life of this radical it was similarly assumed that at 50 per cent. inhibition it is of the order of the time between two collisions with nitric oxide.

radicals might unite in a binary collision to form an activated association product of relatively long life.

The decomposition of ethane provides a most interesting contrast with that of diethyl ether. Both the mean chain length and the plot of the quantity $(p - p_{\infty})/(p_0 - p_{\infty})$ against the nitric oxide concentration are quite independent of the ether pressure. Thus the inhibiting process must be competing with one which itself does not depend on the pressure, and this can only be the unimolecular decomposition of the radical with which the nitric oxide combines. It seems probable that one link in the

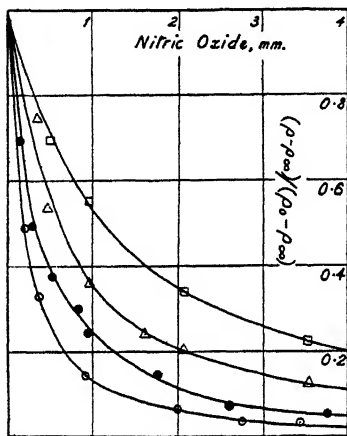


FIG. 2.—Showing how the course of the "inhibition curve" in the thermal decomposition of ethane varies with the ethane pressure. (\square 454 mm.; \triangle 300 mm.; \bullet 100 mm.; \odot 57 mm. Temperature, 600°C .)

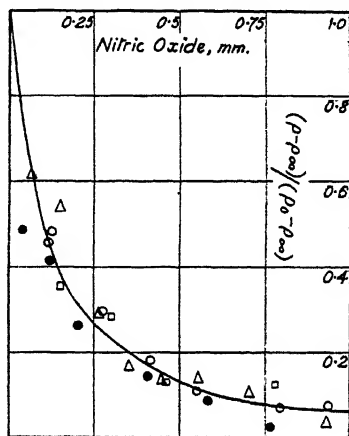


FIG. 3.—Showing that the course of the "inhibition curve" in the thermal decomposition of diethyl ether is independent of the ether pressure. (\triangle 400 mm.; \bullet 200 mm.; \odot 103 mm.; \square 51 mm. Temperature, 504°C .)

chain is the relatively slow decomposition⁴ of a large radical $\text{CH}_2 \cdot \text{O} \cdot \text{C}_2\text{H}_5$.

The activation energy of the chain-free decomposition of ethane has the unusually high value of 74,500 cal. Although this may be numerically quite near the energy required to break the carbon-carbon bond, it does not mean that more than a small fraction of primary processes yield radicals, nor affect the corollary that the absolute chain length is high. For the activation energy is distributed in about fourteen square terms, and there may well be only a very small probability that, before the molecule is deactivated or decomposes by rearrangement, the energy will become localised in one bond, as it must if this bond is to be broken.

⁴ Rice and Herzfeld, *J. Amer. Chem. Soc.*, 1934, 56, 284.

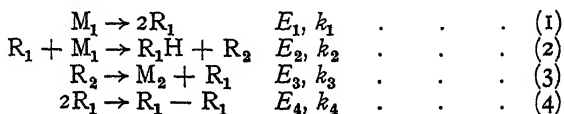
THE DECOMPOSITION OF HYDROCARBONS INDUCED BY FREE RADICALS.

BY F. O. RICE AND O. L. POLLY.

Received 10th February, 1939.

1. Introduction.

On the basis of the free radical theory proposed by one of us,¹ the thermal decomposition of a pure organic compound occurs through a primary rupture of a carbon-carbon bond, followed by a chain reaction which is terminated finally by recombination or disproportionation of the chain radicals. We can represent this schematically by the following four equations:



In this simplified scheme, the substrate molecule M_1 decomposes into the radical R_1 , which is the small chain radical, and the chain ends by recombination of this radical with itself; the E 's and k 's represent the activation energies and velocity constants of the respective reactions. Depending on the values of these constants, the chain might also end by a cross combination of R_1 and R_2 :



The recombination of the two large radicals,



seems improbable in a great many cases on chemical grounds, and will not be considered here. Independently of how the chain starts or stops, it is clear that if the average length is greater than 20 or 30 cycles, the main chemical products of the reaction will be the two substances R_1H and M_2 , accompanied by small quantities of other products whose nature will be determined by the chain stopping reactions. When this scheme is subjected to experimental test, by comparing the predicted chemical products with those found experimentally, there is good agreement for a wide variety of chemical compounds, even for quite complicated molecules.²

This simplified scheme does not give a complete picture of the thermal decomposition of organic molecules because, in general, radicals other than the chain carriers are produced in the primary decomposition; this, however, is not important from either the chemical or kinetic standpoint, because any other radical will disappear after one fruitful collision with the substrate, and be replaced by a chain carrier.

¹ (a) J. Rice, *Am. Chem. Soc.*, 1931, **53**, 1959; (b) Rice and Herzfeld, *ibid.*, 1934, **56**, 284; (c) Rice and Rice, *The Aliphatic Free Radicals*, The Johns Hopkins Press, 1935.

² J. Marschner, *Ind. Eng. Chem.*, 1938, **30**, 554.

According to this scheme, thermal organic decompositions would be divided into two kinds, represented by (A) reactions (1), (2), (3), and (4), or (B) reactions (1), (2), (3), and (5). Whether the A or the B scheme is followed in any particular case will depend on the stability of the large radical R_2 ; most large radicals are unstable and easily decompose to give a small radical and a molecule, so that we would expect most organic decompositions to follow scheme A in which the chain ends by recombination of the small radicals. However, some large radicals are stabilised by resonance or some peculiarity of chemical structure, and when the removal of a hydrogen atom from an organic molecule produces one of these radicals, we would expect the decomposition to follow scheme B.

2. Kinetics.

On the basis of the free radical theory, it follows that we may replace or augment reaction (1) by some other source of free radicals, either thermal or photochemical. We may therefore write a primary reaction



and we shall consider the case in which this reaction is the primary source of free radicals; the conditions are such that the rate of reaction (1) is sufficiently slow that it may be neglected or allowed for by a correction factor.

If we conduct the decomposition at a temperature such that there is a slow decomposition of M_0 , we can apply the usual treatment for steady state conditions: the following applies to scheme A where the reactions considered are (7), (2), (3), (4);

$$k_0[M_0] = k_4[R_1]^2 \quad . \quad . \quad . \quad . \quad (8)$$

$$k_2[R_1][M_1] = k_3[R_2] \quad . \quad . \quad . \quad . \quad (9)$$

$$[R_1] = \sqrt{[M_0]} \sqrt{\frac{k_0}{k_4}} \quad . \quad . \quad . \quad (10)$$

and
$$\frac{d[M_1]}{dt} \cong k_2 R_1 M_1 = [M_1][M_0]^{\frac{1}{2}} k_2 k_0^{\frac{1}{2}} / k_4^{\frac{1}{2}} \quad . \quad . \quad (11)$$

Making the assumptions of Rice and Herzfeld concerning the values of the E 's and k 's we obtain

$$\frac{d[M_1]}{dt} \cong 10 k_0^{\frac{1}{2}} M_0^{\frac{1}{2}} M_1 e^{-\frac{2E_2 + E_4}{2RT}} \quad . \quad . \quad . \quad (12)$$

In an exactly similar manner, scheme B gives

$$\begin{aligned} \frac{d[M_1]}{dt} &\cong [M_1][M_0] k_0 k_2 k_3 / k_4 \\ &= 10 k_0^{\frac{1}{2}} M_0^{\frac{1}{2}} M_1^{\frac{1}{2}} e^{-\frac{E_2 + E_3 - E_4}{2RT}} \quad . \quad . \quad (13) \end{aligned}$$

On the other hand, if we conduct the decomposition at a temperature such that the decomposition of M_0 is very rapid and is substantially completed in the range 0.01-4 seconds, we cannot apply the usual steady

state treatment.* The rate of production, n , of free radicals, produced by (7) may be expressed by the equation

$$n = n_0 e^{-\frac{t^2}{t_0^2}} \quad (14)$$

where n_0 is the maximum rate at time t_0 .

The total number of radicals produced is :

$$x_0 = \int n dt = n_0 t_0 \sqrt{\pi} \cong n_0 t_0 \sqrt{\pi} \quad (15)$$

The rate of the overall uncatalysed reaction (scheme A) as determined by reactions (1), (2), (3), and (4) is given by

$$-\frac{dx_1}{dt} = x_1^{\frac{1}{2}} \sqrt{\frac{k_1 k_2^2}{k_4}} = x_1 \sqrt{\frac{k_1 x_1 k_2^2}{k_4}} = x_1 \sqrt{\frac{n_1 k_2^2}{k_4}} \quad (16)$$

The total number of substrate molecules decomposed is,

$$\begin{aligned} \int x_1 \sqrt{\frac{n_1 k_2^2}{k_4}} dt &= x_1 \sqrt{\frac{k_2^2}{k_4}} \int \sqrt{n} dt = x_1 \sqrt{\frac{k_2^2}{k_4}} \sqrt{n_0 2\pi} t_0 \\ &= x_1 x_0^{\frac{1}{2}} \sqrt{\frac{k_2^2}{k_4}} \pi^{\frac{1}{2}} \sqrt{2} t_0 \cong 2x_1 \sqrt{x_0 k_2} \sqrt{k_4} t_0 \quad (17) \end{aligned}$$

The chain length is given by,

$$\frac{\text{Number of substrate molecules decomposed}}{x_0} = \lambda = \frac{x_1}{\sqrt{x_0}} 2k_2 k_4^{\frac{1}{2}} t_0^{\frac{1}{2}} \quad (18)$$

For scheme B, by following the same method, we obtain,

$$\lambda = \sqrt{\frac{x_1}{x_0}} \sqrt{\frac{k_2 k_3}{k_4}} \sqrt{t_0}$$

3. Experimental Method.

The work was done in a static system in which provision was made to mix the substrate with known amounts of promoter; the mixture was then passed rapidly into a reaction vessel, held at a temperature such that the substrate either did not decompose, or decomposed only slowly. In such experiments, it is necessary to pass a known amount of the mixture into the reaction vessel; this enables us to calculate the initial pressure which cannot be obtained experimentally because of the very rapid reaction occurring immediately the gases enter the reaction bulb. A sketch of the apparatus is given in Fig. 1, in which A and B are bulbs to contain the substrate and promoter, and R is a quartz reaction vessel which was fitted in a suitable furnace having the temperature controlled to about 1° C. The mixing vessel M enabled us to make up accurately known mixtures of substrate and promoter, and then to displace the total mixture into the bulb R. By comparing the observed pressure on the manometer with that calculated, the amount of induced decomposition could be found. It was necessary to make a small correction for the decomposition of the promoter and sometimes, in the higher range of temperature, we had also to correct for a slow decomposition of the substrate. We checked our values for the calculated pressure by putting various pure gases into the mixing bulb and displacing them into the reaction bulb under conditions of temperature and pressure similar to those in our experiments.

It should be mentioned that it is not satisfactory to conduct the experiment by connecting the reaction vessel with the mixing bulb and allowing

* The following treatment was worked out by Professor Karl Herzfeld at the Johns Hopkins Conference held at Gibson Island, July, 1935.

the pressures to equalise. The rapid chain reaction that is induced in the reaction vessel may cause a rapid increase in pressure during the first two or three seconds, and result in some partially decomposed gas being driven

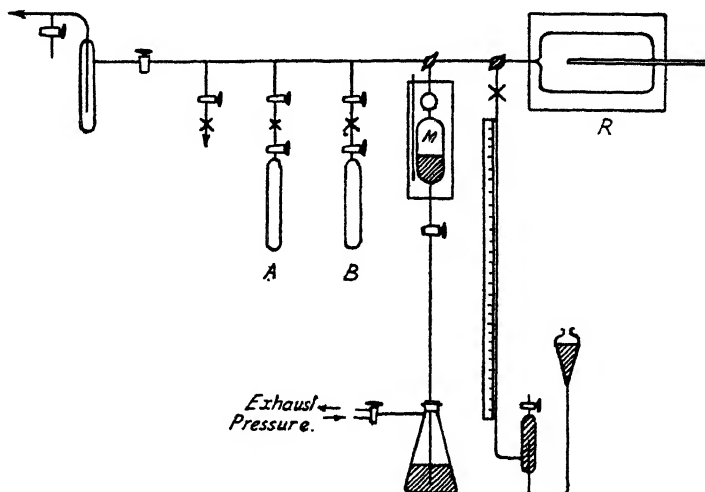


FIG. 1.

back into the mixing vessel. If the pressures are not allowed to equalise, P_0 can be calculated correctly, but we have found that the displacement method is more convenient.

4. The Initial Rate.

We first performed experiments with this apparatus using a substrate which was purified with the greatest care possible. The rate of decomposition of the substrate without any additions was first measured by taking a measured volume in the mixing bulb, and displacing it into the reaction vessel. In this way we could calculate an initial pressure and also obtain a value by extrapolating our measured values of P back to $t = 0$. In spite of every care in the purification of the substrate, we obtained very erratic results; occasionally the calculated and extrapolated values of P_0 would be the same, but in most experiments, the extrapolated value would be greater by 10-30 mm. We finally traced this effect to minute quantities of oxygen which were extremely difficult to remove. However we found that we could effectively remove this oxygen effect by preheating the "pure" substrate in the mixing bulb to about 200° C. for a few minutes. When the substrate was treated in this way, the calculated and extrapolated values of P_0 agreed within our experimental error of ± 2 mm.

In view of these effects, it seemed best to investigate first the oxygen effect, and in the following section we give some of our experimental results with *n*-butane.

5. Discussion and Results.

In Table I we give a typical series of experiments with *n*-butane. In this series the pure substrate decomposes, and so there is a slow increase in pressure after the rapid initial reaction. By measuring the pressure increase during the first few minutes and extrapolating to $t = 0$, we obtained the apparent initial pressure P_0' and the difference between this

and the initial pressure P_0 calculated from the mixing bulb, gave us a measure of the induced decomposition, after making a small correction for the oxygen.

The chain length increases markedly with temperature; below 400° C., the chains, in the case of hydrocarbons, do not extend beyond one

TABLE I.—SENSITISED DECOMPOSITION OF *n*-BUTANE BY OXYGEN. λ IS THE NUMBER OF MOLECULES OF BUTANE DECOMPOSED PER MOLECULE OF OXYGEN.

Exp. No.	mm. O ₂ x_0	mm. <i>n</i> -C ₄ H ₁₀ x_1	Temp. °C.	λ	x_0/x_1
37J25·4	0·92	297	508	21·7	0·070
37J25·5	1·54	297	508	17·5	0·073
37J25·6	2·39	299	508	14·1	0·074
37J25·7	3·17	299	508	10·9	0·065
37J25·8	3·16	298	508	12·2	0·074
37J25·9	3·98	299	508	10·5	0·070
37A11·4	0·054	388	516	154	0·093
37A31·4	0·753	401	502	31·7	0·070
37A31·5	1·01	499	502	33·8	0·070
37A31·8	1·21	600	502	32·9	0·062
37A31·10	0·61	296	502	35·5	0·097
37A31·12	0·41	197	502	24·7	0·082
37A31·14	0·40	197	502	27·1	0·089
37A31·15	0·20	98	502	29·2	0·136

unit, whereas in the region in which the hydrocarbon is decomposing rapidly, small additions of oxygen produce chains up to several hundred links. Similar results are obtained by the addition of unstable compounds such as azomethane, and a full account of the work will appear in a forthcoming publication.

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THE REACTION OF HYDROGEN ATOMS WITH PROPANE AND THE MECHANISM OF THE PARAFFIN DECOMPOSITIONS.

By E. W. R. STEACIE AND N. A. D. PARLEE.

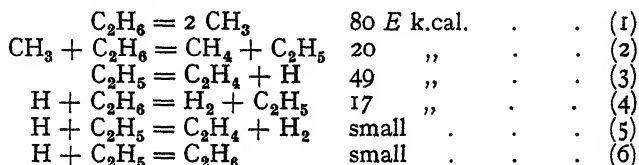
Received 23rd January, 1939.

Introduction.

The Rice theory of the free radical decomposition of organic compounds, and the specific Rice-Herzfeld mechanisms for certain compounds have given a great stimulus to the investigation of organic decomposition reactions. In particular, much work has been done on the paraffin decompositions,¹ especially that of ethane.

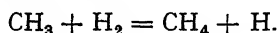
¹ See Steacie, *Chem. Reviews*, 1938, **22**, 311 for references.

The Rice-Herzfeld mechanism ² for the ethane decomposition involves as the main steps the reactions :



The activation energy given for reaction (1) is the experimental value for the free radical split. The remaining activation energies were frankly assigned by Rice and Herzfeld to make the scheme agree with experiment. Various tests of the scheme have been made by investigating the part reactions.

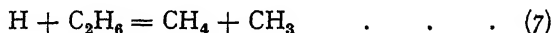
Patat and Sachsse ^{3,4} used the *ortho-para* hydrogen conversion to measure the stationary hydrogen atom concentration produced by the above reactions and by the reaction



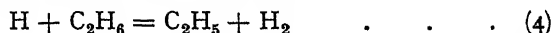
They found a value for the hydrogen atom concentration about 1000 times smaller than that predicted by the Rice-Herzfeld mechanism.

Investigations of the reactions of deuterium atoms with ethane by Steacie and Phillips,⁵ and by Trenner, Morikawa, and Taylor⁶ lead to the conclusion that E_4 is about 9 k.cal. This removes the disagreement between Patat and Sachsse's results and the Rice-Herzfeld scheme in so far as the hydrogen atom concentration is concerned, but with the new value of E_4 the scheme no longer predicts a first order rate or the correct value of the activation energy of the overall reaction.^{7,8} It is therefore apparent that the Rice-Herzfeld mechanism for the decomposition of ethane is untenable in its present form, but there is some evidence that free radical mechanisms may be valid for the decomposition reactions of the higher paraffins.⁹

There is, however, a much more serious apparent discrepancy between the Rice theory and experiment which arises from the investigation of the reaction of hydrogen atoms with ethane. Trenner, Morikawa, and Taylor found that methane was produced in this reaction, and concluded that the reaction



had an activation energy several k.cal. lower than



The production of methane in the reaction of hydrogen atoms with ethane was confirmed by Steacie.¹⁰ Further information about the relative rates of reactions (4) and (7) comes from the investigation of the mercury

² Rice and Herzfeld, *J. Am. Chem. Soc.*, 1934, **56**, 284.

³ Patat and Sachsse, *Z. Elektrochem.*, 1935, **41**, 493.

⁴ Patat and Sachsse, *Z. physik. Chem., B*, 1935, **31**, 79.

⁵ Steacie and Phillips, *J. Chem. Physics*, 1936, **4**, 461.

⁶ Trenner, Morikawa, and Taylor, *ibid.*, 1937, **5**, 203.

⁷ Steacie and Philips, *ibid.*, 275.

⁸ Storch and Kassel, *J. Am. Chem. Soc.*, 1937, **59**, 1240.

⁹ For a summary of the evidence see ¹ and Steacie, *Can. Chem. and Process Ind.*, 1938, **22**, 325.

¹⁰ Steacie, *J. Chem. Physics*, 1938, **6**, 37.

$$\begin{array}{rcll}
\text{C}_2\text{H}_6 + \text{Hg}(^3P_1) & = & \text{C}_2\text{H}_5 + \text{H} + \text{Hg}(^1S_0) & \\
\text{H} + \text{C}_2\text{H}_6 & = & \text{C}_2\text{H}_5 + \text{H}_2 & (4) \\
\text{H} + \text{C}_2\text{H}_6 & = & \text{CH}_4 + \text{CH}_3 & (7) \\
2\text{CH}_3 & = & \text{C}_2\text{H}_6 & (8) \\
\text{CH}_3 + \text{C}_2\text{H}_5 & = & \text{C}_3\text{H}_8 & (9) \\
2\text{C}_2\text{H}_5 & = & \text{C}_4\text{H}_{10} & (10) \\
2\text{H} & = & \text{H}_2 & (11) \\
\text{H}_2 + \text{Hg}(^3P_1) & = & 2\text{H} + \text{Hg}(^1S_0) & (12)
\end{array}$$

¹⁵ Rice and Teller, *J. Chem. Physics*, 1938, 6, 489.

The Reaction of Hydrogen Atoms with Propane.

The reaction was investigated by the Wood-Bonhoeffer method, an electrical discharge being employed to produce atomic hydrogen. The apparatus was similar to that used in previous investigations.¹⁶ The products of the reaction were removed from the flow system by two liquid air traps, one of which was empty, while the other contained silica gel. In this way it was possible to recover all the hydrocarbons, including methane, while almost all the hydrogen passed the traps.

The resulting hydrocarbon mixture was analysed by means of a small-capacity low-temperature distillation apparatus of the Podbielniak type. Checks on the unsaturates were also made by conventional gas analysis methods.

The average atom concentration in the experiments was about 20 per cent. of the total hydrogen. Full details of collision yields, etc., will be given in a later paper. For our present purpose the main interest attaches to the analyses of the products of the reaction at different temperatures, and these results are given in Table I.

TABLE I.—THE PRODUCTS OF THE REACTION OF HYDROGEN ATOMS WITH PROPANE.

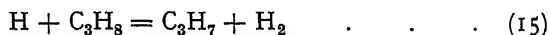
Temperature, °C.	$\frac{H_2}{C_3H_8}$ Ratio.	Products, Mole Per Cent.				
		CH ₄ .	C ₂ H ₆ .	C ₂ H ₄ .	CO ₂ .	C ₃ H ₈ .
30	8	23.2	—	—	1.0	75.8
	8	21.8	—	—	0.5	77.7
	8	18.0	—	0.7	0.3	81.0
	8	22.5	—	—	0.5	76.0
	8	19.2	—	—	0.5	80.3
	16	25.8	—	—	0.3	73.9
100	4	12.8	—	—	0.3	86.9
	8	13.5	3.0	0.8	0.5	82.2
170	8	9.7	11.7	1.4	0.6	76.6
	8	9.2	12.5	2.0	0.6	75.7
	8	8.8	10.1	1.5	0.6	79.0
	8	8.8	12.2	1.8	0.6	76.6
250	8	7.1	14.3	3.2	0.7	74.5
	8	5.7	14.0	3.2	0.6	76.3

The results of Table I are in agreement with two experiments made by Trenner, Morikawa, and Taylor which indicated practically exclusively methane as a product at room temperature, together with ethane at higher temperatures.

Discussion.

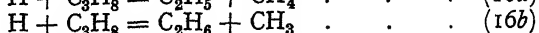
The Primary Reaction.

There are obviously two possibilities for the primary step, the abstraction of a hydrogen atom,



¹⁶ Steacie, *Can. J. Research, B*, 1937, **15**, 264.

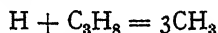
or a chain splitting reaction,



Preliminary results on the mercury photosensitised reaction of hydrogen and propane show that hydrogen and hexane are the main products, and therefore suggest that (15) is the primary step in this case, although the possibility of the occurrence of (16) here cannot be ruled out on this evidence alone.

It may be remarked that there is a very definite parallelism between the reactions of hydrogen atoms with ethane and with propane in so far as a comparison of the results of mercury photosensitisation and of the Wood-Bonhoeffer method is concerned. In both cases large amounts of higher paraffins are obtained by mercury photosensitisation (propane and butane from ethane, and hexane from propane), while by the discharge-tube method only lower paraffins are obtained. The difference between the results of the two methods is, of course, due to the difference in the hydrogen-atom concentration, and in the total pressure. In the mercury photosensitisation method the low hydrogen-atom concentration and relatively high pressure favour recombination of radicals rather than their further reaction with hydrogen atoms. On the other hand, in the discharge-tube method, the low pressure and high hydrogen-atom concentration make recombination to form higher hydrocarbons unlikely.

The possible primary step



is ruled out on thermochemical grounds.

Secondary Reactions at Low Temperatures.

The main feature of the results at 30° C. is the absence of ethane and ethylene in the products, and the large production of methane.

If the primary reaction were (16b), the results could not be explained on the assumption that the ethane formed disappears by (7), since the reaction of hydrogen atoms with ethane at this temperature is not rapid enough to enable the ethane formed to be completely destroyed. Reaction (16b) can therefore be ruled out as a primary step. In any case (16b) is intrinsically less likely than (16a), since if a C—C bond is to be broken it is much more likely that the bond nearest to the approaching hydrogen atom shall split, giving methane and an ethyl radical, *i.e.*, (16a).

If the primary reaction is (16a), then the ethyl radicals produced must react to form methane without the intermediate formation of ethane. The only possibility seems to be the reaction discussed above, *viz.*,



followed by (14).

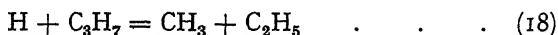
If the primary reaction is (15), then the propyl radicals produced must disappear without the formation of ethane. We cannot postulate the decomposition of the propyl radical by the reaction



since all the evidence indicates that it is stable at room temperature. In any case the assumption of (17) would lead to new difficulties, since it has been shown¹⁷ that the main product of the reaction of hydrogen

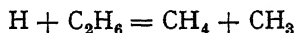
¹⁷ v. Wartenberg and Schultze, *Z. physik. Chem.*, B, 1929, 2, 1.

atoms with ethylene is ethane, and neither ethylene nor ethane occur as products. It must therefore be concluded that if the primary reaction is (15), the propyl radicals produced disappear by a reaction analogous to (13), *viz.*,



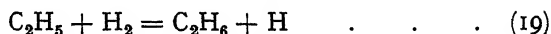
If this is the case, then the ethyl radicals formed by (18) must disappear by (13).

It follows that, irrespective of whether the primary reaction is (15) or (16), the results can only be accounted for by the assumption that reaction (13) occurs readily. The present results therefore furnish strong evidence for the occurrence of (13), and obviate the necessity of assuming reactions of the type



The evidence from mercury photosensitisation experiments with propane also suggests that the analogous reaction to (13) also occurs with the propyl radical.

It may be noted that in considering the low temperature results the possible reaction of ethyl radicals with molecular hydrogen,

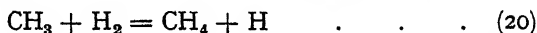


must be ruled out since it would lead to ethane formation.

Secondary Reactions at Higher Temperatures.

At higher temperatures methane production is diminished, and ethane and ethylene make their appearance. The production of ethylene is undoubtedly to be ascribed to the decomposition of the propyl radical at higher temperatures by reaction (17). This is in agreement with the fact that the propyl radical can be detected in photodecompositions at ordinary temperatures by the Paneth technique,¹⁸ but cannot be detected in thermal decomposition reactions at higher temperatures.¹⁹ Bawn estimates an activation energy for reaction (17) of from 10 to 30 k.cal.²⁰ Ethylene may also be formed in part by reaction (5).

The appearance of ethane at higher temperatures is presumably to be ascribed to the occurrence of reaction (19). Leermakers²¹ estimates an activation energy of 15 k.cal. or more for this reaction. This estimate, however, is probably somewhat high, since the companion reaction



occurs to a measurable extent at temperatures of 160° C. and higher,^{6, 22, 23} and Taylor¹⁴ estimates that it has an activation energy of 9 ± 2 k.cal. An activation energy of the same order of magnitude for (19) would account for the ethane production in the present instance.

The authors wish to express their indebtedness to the National Research Council of Canada for financial assistance.

¹⁸ Pearson and Purcell, *J. Chem. Soc.*, 1936, 253.

¹⁹ Paneth and Lautsch, *ibid.*, 1935, 380.

²⁰ Bawn, *Trans. Faraday Soc.*, 1938, 34, 598.

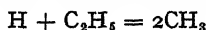
²¹ Leermakers, *J. Am. Chem. Soc.*, 1933, 55, 4508.

²² Morikawa, Benedict, and Taylor, *J. Chem. Physics*, 1937, 5, 212

²³ Taylor and Rosenblum, *ibid.*, 1938, 6, 179.

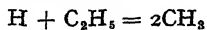
Summary.

The reactions of ethane and of ethyl radicals with hydrogen atoms are reviewed, and the importance of the reaction

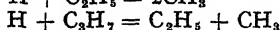


from the standpoint of the Rice theory is emphasised.

Experiments on the reaction of hydrogen atoms with propane by the Wood-Bonhoffer method are described. The products of the reaction are methane, ethane, and ethylene at high temperatures, but methane is the only product at low temperatures. The results are discussed, and it is concluded that they offer strong evidence that the reactions



and



occur readily at room temperature.

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ON THE PYROLYSIS OF 2-CARBON AND 3-CARBON PARAFFIN AND OLEFINE HYDROCARBONS.

BY MORRIS W. TRAVERS.

Part I. Equilibrium Mixtures.

Received 19th January and amended as presented on 17th April, 1939.

When paraffin hydrocarbons are heated, the first reaction, and possibly the only reaction in which they take part in absence of olefines, results in the formation of the corresponding olefine with hydrogen. The process becomes very rapid in the neighbourhood of 600°. The statement often made that the process is homogeneous appears to be entirely unsupported by experimental evidence, and experiments carried out in my laboratory suggest that it is fairly strongly catalysed by silica surfaces¹ (p. 333). Pure olefines undergo condensation at temperatures above 300° even in silica apparatus, but the process appears to be catalysed by the surface. In the neighbourhood of 600° the surface reactions yield hydrogen, which results in the formation of paraffins, the subsequent changes following the course which I propose to discuss.

If we study the pyrolysis of the 2-carbon hydrocarbons, starting from ethane, and carry out our experiments in silica apparatus, the neighbourhood of 600°, we find that following the primary decomposition process, which results in the rapid approach to equilibrium in the system represented by the equation,



a homogeneous reaction, or reactions, sets in which results in the formation of methane and of aromatic condensation products. As it appeared probable that these changes were independent of the pro-

¹ Travers and Pearce, *J. Chem. Ind.*, 1934, 53, 321.

cesses leading to the establishment of equilibrium in the ethane, ethylene, hydrogen system, as represented by equation (1), we decided to eliminate the complication arising from them by starting with equilibrium mixtures of ethane, ethylene, and hydrogen, instead of with the pure hydrocarbons.^{1, 2} The equilibrium reactions at 600° operate so rapidly as to maintain a condition approaching closely to that of equilibrium in the ethane-ethylene-hydrogen system, and merely form a background to the processes leading to the formation of methane and condensation products. We refer to them, therefore, as the *background reaction*. A recent reviewer³ has credited us with introducing a new principle under this term, but it is merely a convenient way of representing a well-known fact.

I may now refer to a difference in the method which we use,¹ and that which is in common use in such investigations, which can be illustrated in the following manner. We start with a mixture of a C_2H_6 , b C_2H_4 , and c H_2 , and we obtain a mixture of a' C_2H_6 , b' C_2H_4 , c' H_2 , d CH_4 , and e of non-volatile condensation products. In the neighbourhood of 600° the ratio $b \times c/a$, originally corresponding to equilibrium conditions, remains sensibly constant. Now if, following the usual practice, we withdraw a sample of the volatile constituents from the reaction vessel, we can determine the relative proportions $a'/b'/c'/d$, but we do not know the relationship of a' , b' , c' and d to a and b , which is really what we want to know.

Nearly a hundred experiments with ethane-ethylene-hydrogen equilibrium mixtures have been carried out in my laboratory. Even in our earliest attempts to analyse the results, in which we considered the formation of methane and the formation of condensation products as separate processes, it was clear that there was no direct connection between the rates of the processes involved in the pyrolysis and the concentration of the ethane. We did, however, succeed in establishing a

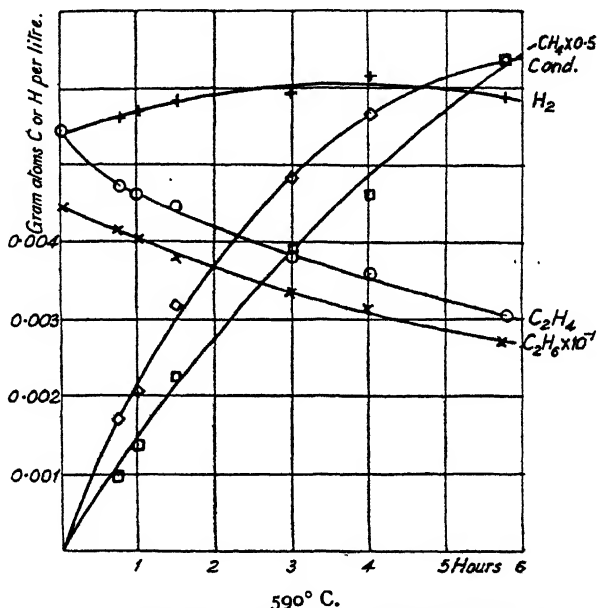


Fig. 1.—Pyrolysis of equilibrium mixture containing—

Ethane	0.04456	} Gram atoms C or H per litre.
Ethylene	0.00544	
Hydrogen	0.00536	

² Travers, *Trans. Faraday Soc.*, 1937, **33**, 735.

³ Steacie, *Chemical Reviews*, 1938, **33**, 311.

connection between the rates of formation of the methane and of the condensate, considered as separate processes, with the concentration of the ethylene¹ (p. 326). This was afterwards abandoned. We also gave an explanation, which still holds good, of why it was that methane and condensation products were not primary products of the pyrolysis of pure ethane. However, again reviewing the whole of the data, it seemed clear that the formation of methane and of condensation products was probably dependent on a single time-determining process, and, therefore, the rate at which they were formed was exactly equivalent to the rate of disappearance of 2-carbon hydrocarbon, that is, either of ethane or of ethylene or of both together. Actually the relationship represented by

$$-d(C_2H_6 + C_2H_4)/dt = d(CH_4 + \text{condensate})/dt = k(C_2H_6)(C_2H_4) \quad (2)$$

held good for the very wide range of our experiments.

Figs. 1 and 2 represent the rates of disappearance of reactants, and

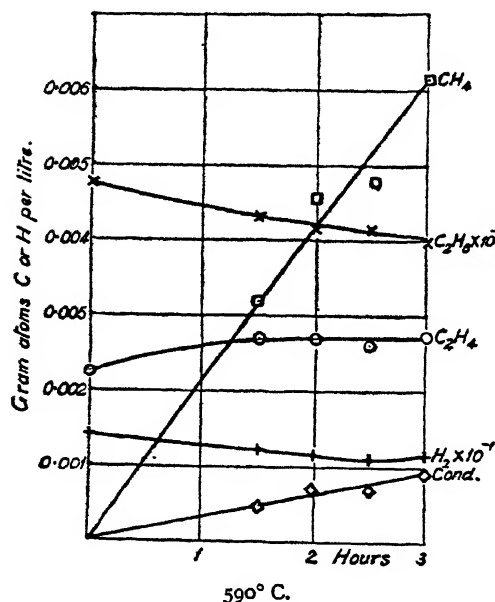


FIG. 2.—Pyrolysis of equilibrium mixture containing—

Ethane	. 0.04736	} Gram atoms C or H per litre.
Ethylene	. 0.00264	
Hydrogen	. 0.01215	

appearance of resultants, in two ethane-ethylene-hydrogen equilibrium mixtures at 590°. It is quite clear that the equation (2) represents only a single time-determining step in a series of complex processes, the exact nature of which we are not in a position to analyse.

Of course, it is impossible to follow such complex changes by any mathematical expression; but as the whole course of the process is followed by analytical methods, it is a simple matter to follow the changes by a computational method, and to calculate the value of the velocity constant for each time interval. This method has the advantage that it is possible to detect the effect of

errors introduced by temperature lag, if any, and to determine the true variation of the value of the velocity constant with time, which the usual method of integrating between time 0 and t does not give.

The ratio (Methane)/(Condensation products) varies over wide limits. With equilibrium mixtures with high hydrogen content there is practically no condensate formed at all, and the product is methane alone. Some experiments carried out by Dr. Pearce and myself with mixtures containing a very large quantity of hydrogen appeared to show that, under these conditions, a surface reaction operated. We could not

interpret the results, which were not published. With mixtures of low hydrogen content the value of the ratio appears to approach unity, that is, one carbon atom appearing as condensate for each carbon atom appearing as methane. I shall refer to this point again later.

After finishing the work on the ethane-ethylene-hydrogen mixtures, a series of experiments was carried out on propane-propylene-hydrogen equilibrium mixtures.⁴ These were very difficult and laborious, and experimental results are relatively few. Fig. 3 represents the rate of disappearance of reactants, and appearance of resultants in such a series of experiments, which is characteristic of them all. I interpret them in the following way.

It seems to be perfectly clear that, apart from the propane-propylene-hydrogen background process, the primary pyrolytic process involves the formation of ethylene and methane only. The ethylene and hydrogen then react to form ethane, which is not produced in the primary process, since the graph shows that the initial rate of formation is small, and is self-accelerated. The ethane and ethylene then react to produce more methane and condensate, the initial rate

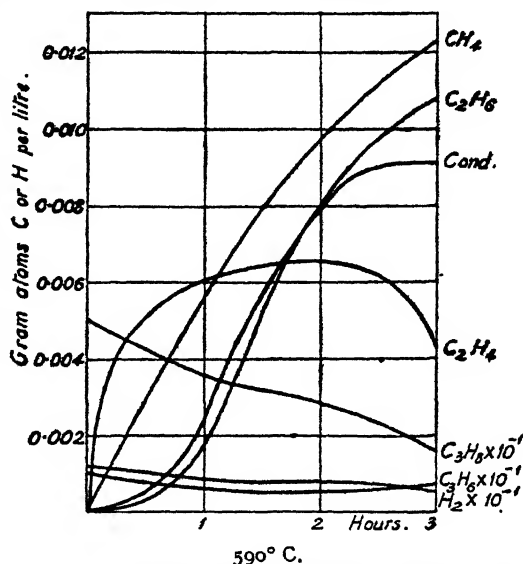


FIG. 3.—Pyrolysis of equilibrium mixture containing—

Propane	0.04986	} Gram atoms C or H per litre.
Propylene	0.01014	
Hydrogen	0.01125	

of formation of the latter also being small and self-accelerated. Now if the above analysis is correct, the sum S of the quantities

$$\text{Ethylene} + \text{Ethane} + \text{Condensate} \quad . \quad . \quad . \quad (3)$$

for the shortest time interval gives a fairly accurate estimate of the amount of ethylene formed and transformed in the same interval. Only a small quantity of the methane produced in the same time interval is formed, otherwise than in the reaction in which the ethylene is formed as a primary pyrolytic product. This extra small quantity of methane is not larger than the equivalent of the condensate produced. The value of the ratio, $S/(\text{Methane formed})$, should then give a measure of the initial relationship $(\text{Ethylene formed})/(\text{Methane formed})$, and the data in gram atoms of carbon in all six series of experiments show that this is nearly 2/1. That is to say, the initial process of pyrolysis involves the formation of one molecule of ethylene for one molecule of methane.

⁴ Travers, *Trans. Faraday Soc.*, 1937, 33, 751.

This would suggest that the change was represented by the equation,



particularly in the experiments for longer periods, was a little greater than 2 (Table I, Col. 8). In the other portion, the ethylene was estimated; but the remaining paraffin hydrocarbon, when burned over copper

TABLE I.*

Serial.	Minutes.	H ₂ .	C ₂ H ₄ .	CH ₄ .	R.	$\frac{CH_4+R}{2}$.	$\frac{CO_2}{C_2H_4+C_2H_6}$.	$\frac{CO_2}{C_2H_6}$.	C ₂ H ₆ .	$\frac{C_2H_6 \times H_2}{C_2H_6}$.
11	10	105	118	18	—	—	—	—	1876	0.0046
12	10	127	126	12 _s	—	—	—	1.998	1868	0.0060
29	15	119	139	14	6 _s	10	1.983	2.000	1851	0.0063
13	20	172	167 _s	18 _s	—	—	2.000	2.000	—	—
28	25	133 _s	141	22 _s	4	13	1.997	2.003	1846	0.0072
10	25	154	164	35	—	—	2.005	2.000	—	—
6	30	192	200	33 _s	5 _s	14 _s	1.996	2.004	1780	0.0152
7	35	204	189	55	12 _s	34	2.004	1.998	1777	—
1	40	186	176 _s	56	30	43	—	—	—	—
18	40	200	194	62	23	42 _s	—	1.997	1764	0.0145
17	44	—	179	—	—	—	—	1.992	1781	0.0131
15	46	224	—	65	—	—	2.012	2.004	—	—
4	60	224	193	92 _s	—	—	2.004	1.986	—	—
16	60	240	246	111	49	80	2.004	2.012	1670	0.0250
2	70	240 _s	177 _s	98	—	—	—	—	—	—
21	70	227	197	121	57 _s	89	1.986	1.997	1714	0.0185
22	70	232	—	122 _s	68	95	—	—	—	—
13	80	253	175	185	59 _s	122	2.013	1.198	1703	0.0184
14	100	250 _s	239 _s	200	75	137	—	2.000	1623	0.0260
15	100	236	228	202	195 _s	173	2.003	2.015	1592	0.0234
23	100	253	206	207	117 _s	162	—	—	1632	0.0226
19	126	233	182	209	78	143	2.016	2.000	1675	0.0179
20	142	234	175	240	75	157	2.010	2.000	1668	0.0174

* Data in g. mols./l. $\times 10^5$. R (non-volatile at -80°) in g. atoms carbon litre $\times 10^5$. $(C_2H_4 \times H_2)/C_2H_6$ in atmospheres. Temperature 590° C.

oxide, gave a ratio as above very close to 2 (Table I, Col. 9). The conclusion is that the gas resulting from pyrolysis contains a little propylene or butylene, not exceeding 0.4 per cent., but no propane.

The results as a whole show that even when the greatest care is taken to treat the reaction vessel in exactly the same manner before each experiment, the amounts of hydrogen and of ethylene are not exactly reproducible. This confirms the conclusion arrived at previously that the primary decomposition process is influenced by surface to a material extent. Certainly, increasing the extent of surface does increase the rate of the primary process,¹ but not to so large an extent as to lead to the conclusion that the effect is catalytic. It is possible that this is a case of radicals being formed at the surface, and the reaction chains being broken at the surface.

The irregularity in the operation of the primary process makes the rate of formation of methane and aromatic condensate together, which is probably the true measure of the rate of the secondary process, somewhat irregular, particularly for the longer time intervals. However, it is quite clear that the secondary process is represented by an S-shaped graph, and that it does not start till ethylene, or possibly ethylene and hydrogen, are present in the gas. It is therefore, correct to make a distinction between the primary and secondary processes involved in the thermal decomposition of ethane.

In Fig. 4, the sum of the quantities of methane and aromatic condensate ($\text{CH}_4 + \text{R}$), are given as half the quantities in gram atoms of carbon, or as equivalents of 2-carbon hydrocarbon disappearing to form methane and condensate. The result shows that, under the conditions of this experiment, the primary and secondary processes soon become of equal importance.

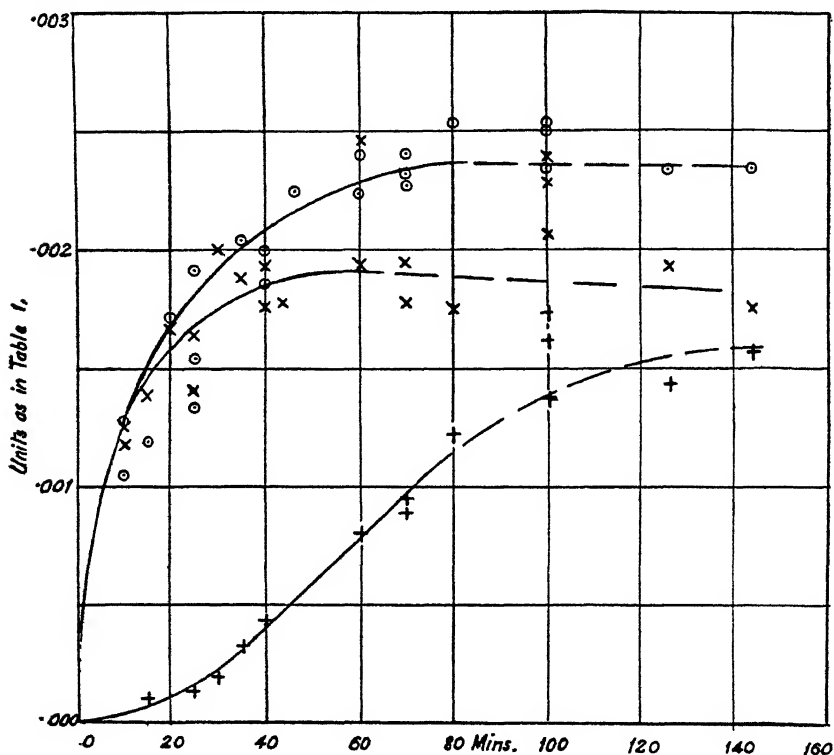


FIG. 4.—The pyrolysis of pure ethane.

H_2 ○ C_2H_4 × $(\text{CH}_4 + \text{R})/2$ +.

Part III. The Influence of Nitric Oxide on the Secondary Decomposition of Ethane.*

By MORRIS W. TRAVERS AND J. A. HAWKES.

Hinshelwood and Staveley have shown that nitric oxide has an inhibiting effect on the changes which give rise to the increase in pressure which takes place when ethane is heated. We do not propose to discuss this work in any detail, but we must point out that the primary decomposition of ethane, and also the primary decomposition of dimethyl-ether, which is also inhibited by nitric oxide, are both materially influenced by surface. It has been shown elsewhere, that the rate of the secondary decomposition of ethane, involving the formation of methane and aromatic condensation products together, is not influenced by surface. However, the ratio

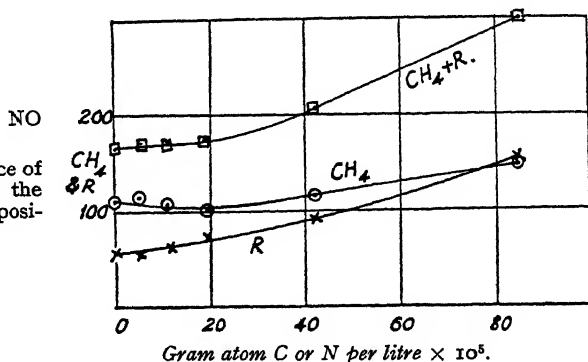
Methane/Aromatic condensation product,

* Presented on 17th April, 1939.

may be influenced by surface, and also by the hydrogen concentration, since it is quite possible that the process involves a great number of steps besides the time-determining step.

To investigate the influence of nitric oxide on the secondary process, we made up a mixture of ethane, ethylene, and hydrogen, such as is produced after heating ethane for an hour under the conditions obtaining

FIG. 5.—Influence of nitric oxide on the secondary decomposition of ethane.



in the experiment described above (Table I, Fig. 4). One sample of this gas was heated for one hour at 590°, in the apparatus used previously, and then other samples, mixed with successively increasing quantities of nitric oxide were treated similarly. The results are shown in Table II and Fig. 5. It is quite clear that the secondary decomposition of ethane is not inhibited by nitric oxide.

According to Hinshlewood and Staveley the fact that nitric oxide inhibits the primary decomposition of ethane to a material extent is

TABLE II.*

NO added.	H ₂ .	CH ₄ .	R.	CH ₄ + R.	C ₂ H ₄ .	C ₂ H ₆ .	$\frac{C_2H_4 \times H_2}{C_2H_6}$
0	Initial						0.0187
	235	0	0	0	185	1640	
0 5 11.5 19.5 42 85	Final						0.0243 0.0240 0.0232 0.0215 — —
	251	110.5	57.5	168	187	1369	
	252	114	57	171.5	184.5	1370	
	246	107	65	172	183	1371	
	226	100	74	174	184.5	1369	
	203	116	92	208	—	—	
	219	148	152	300	—	—	

* NO, H₂, CH₄, C₂H₄ and C₂H₆ in g. mols./l. $\times 10^5$. R (non-volatile at — 80°) in g. atoms C/l. $\times 10^5$. $(C_2H_4 \times H_2)/C_2H_6$ in atmospheres.

taken as evidence that the process is initiated and carried on by a homogenous free radical mechanism at least to the extent to which it is inhibited. It is very astonishing therefore, that neither the formation of methane, nor the formation of aromatic condensate is inhibited by nitric oxide at all. It must, however, be borne in mind, that the evidence that the primary process is homogenous is open to question, and it has been found quite impossible to correlate the data relating to the primary process, and those relating to the necessary reactions involving free radicals,

in such a manner as to furnish any evidence at all that free radicals are involved in the primary decomposition of ethane. Further evidence against the view that the primary decomposition of ethane is initiated by free methyl radicals is put forward in the note contributed to the discussion by Travers and Gray. Since it appears certain that methane and condensation products are not derived from ethane alone, but only from systems containing ethane, ethylene, and consequently hydrogen, and as it is difficult to see how they can be accounted for, without invoking a free radical mechanism, if Hinshelwood and Staveley's views are correct, it is possible that the secondary decomposition is initiated by free methylene radicals. This idea does not, however, seem to be a very satisfactory one.

It may be pointed out in conclusion, that our whole knowledge of the primary decomposition of ethane rests on a comparatively few measurements of the rate of increase in pressure in ethane when heated at constant volume. The data relating to the secondary process are derived entirely from some rather early work carried out in this laboratory. If opportunity offers it is proposed to carry out a much more detailed investigation, using methods developed during the past two or three years. Our knowledge of the pyrolysis of hydrocarbons generally must be based on the study of the ethane-ethylene-hydrogen system, and the importance of the subject would justify the expenditure of a good deal of work upon it.

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ON THE KINETICS OF THE THERMAL DECOMPOSITION OF TETRAMETHYL METHANE (NEOPENTANE).

BY T. J. GRAY AND MORRIS W. TRAVERS.

Presented on 17th April, 1939.

The present investigation was suggested by the results of the examination of the thermal decomposition of the three methyl amines, which have been communicated to the Chemical Society. It was found that in the neighbourhood of 400° the tri- and di-methyl amines decomposed to yield methane, with very little hydrogen, at rates which are almost exactly the same. In each case the critical increment of the process is 58-59 K.cals. The rates of reaction are slowed down by packing the reaction vessel, and accelerated by the addition of helium. There is no difficulty in representing the processes by radical chain mechanisms, and they are doubtless initiated by the formation of free methyl radicals generated in the gas phase.

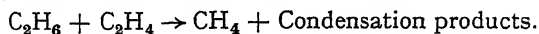
In the case of methylamine, decomposition at a comparable rate does not take place till a temperature one hundred degrees higher is reached, and in this case the initial change does not involve the formation of methane but of hydrogen. Methane, ammonia, and hydrogen cyanide are products of a secondary reaction, and there is some evidence that this involves both the product of primary change, $\text{CH}_2\text{:NH}$, with another molecule of methyl amine.

It was therefore decided to compare the changes which take place when the compounds obtained by replacing the hydrogen atoms in methane by methyl groups were heated, these compounds being represented by the formulæ, $\text{CH}_3\text{.CH}_3$, $(\text{CH}_3)_2\text{CH}_2$, $(\text{CH}_3)_3\text{CH}$, $(\text{CH}_3)_4\text{C}$. The thermal decomposition of ethane will be discussed in the course of

the meeting, and it is only necessary to refer here to the view held by ourselves that it involves two distinct stages, firstly, the primary decomposition process,



and secondly, the process of pyrolysis,



The rate of disappearance of the two-carbon hydrocarbon in the second stage is proportional to the products of the concentrations of the ethane and ethylene, the critical increment of the process being about 55 K.cals. A similar set of relationships has been found to obtain in the case of propane and propylene. The analogy with the behaviour of methyl amine is obvious.

The decomposition of isobutylene and of neopentane had not been studied previously, so we decided to begin with the investigation of the latter compound, which was obtained by treating tertiary butyl chloride with zinc dimethyl. A pure product was obtained boiling at 9.5°. The method of investigation was that described in a paper recently communicated to this Society, by means of which it is possible to carry out an examination of the decomposition of a vapour, without error due to thermal lag, and to follow the rates of decomposition by detailed analytical methods. In experiments carried out so far, only the methane and hydrogen have been measured.

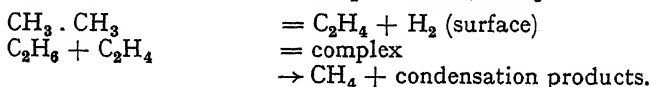
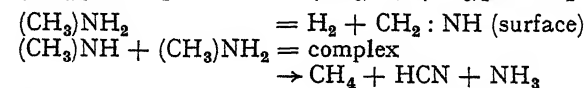
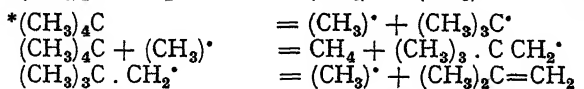
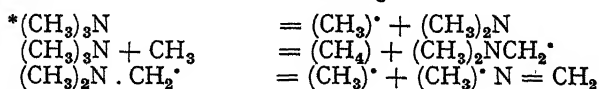
The rate of formation of methane at 500-520° may be represented for an initial period by an expression of 1.5 th. order. However, the rate of formation of methane tends at first to diminish, and then to increase. This may be explained by the fact that the product, or products of decomposition, containing four carbon atoms, and unsaturated, may be more unstable thermally than neopentane itself.

The rate of formation of methane is slowed down by packing the reaction tube. This suggests a mechanism initiated by the formation of free methyl radicals.

The value of the critical increment of the process is estimated at 60 K.cals.

The formation of methane from neopentane and from ethane at comparable rates takes place at approximately one hundred degrees higher temperature in the case of the latter than in the case of the former compound.

The following scheme shows the similarity between the mechanisms of the reactions which we are considering:—



* A little hydrogen is produced in both processes.

That the decomposition process in the case of $(\text{CH}_3)_4\text{C}$ and $(\text{CH}_3)_3\text{N}$ is initiated by the homogeneous formation of free methyl radicals seems to be at least the simplest way of accounting for these phenomena. Consequently, the very different behaviour of $(\text{CH}_3)_3\text{NH}_2$ and $\text{CH}_3 \cdot \text{CH}_3$ makes it difficult to accept the view that the decomposition reactions are initiated by an identical mechanism. What the process is which initiates the decomposition of the latter compound is a little obscure, but it does not seem to be the homogeneous formation of free radicals.

The study of the thermal decomposition of such highly branched hydrocarbon chains is important in view of the known facts relating to antiknock fuels.

The work is being continued.

*The Department of Chemistry,
University of Bristol.*

GENERAL DISCUSSION.*

Prof. C. N. Hinshelwood (*Oxford*) said: One of the questions so far raised is whether the initial step in the decomposition of ethane is homogeneous or not. The influence of the surface may depend very much on the experimental conditions, but may be investigated by the use of packed reaction vessels. Under the conditions of our experiments the decomposition of the hydrocarbons has proved to be homogeneous, except for a few per cent. of surface reaction.

The NO certainly inhibits reactions which the test of surface variation shows to be almost entirely homogeneous. Moreover, it fails to inhibit reactions which are chemically similar but known to be heterogeneous. The decomposition, for example, of HCOOCH_3 into CO_2 and CH_4 , under the conditions of our experiments, is wholly heterogeneous and is influenced by the addition of small amounts of NO. Furthermore, the photolysis of CH_3CHO at 300° , which must be a homogeneous process, has its quantum yield reduced from several hundred to unity by NO. Finally, it may be added, the quantitative kinetics of heterogeneous reactions would be so different that there would be little chance of mistaking them for homogeneous reactions (compare, for example, the contrast of Fig. 2 and Fig. 3 in the paper by Staveley and Hinshelwood).

There is usually a few per cent. of surface reaction even in one described as homogeneous, so that it is obvious that changes in experimental conditions may alter the picture entirely. However, it should be stated that in the work from our laboratory, where reactions are described as homogeneous, the direct test under the actual conditions has been applied.

A certain amount of controversy goes on about alternative primary processes, and apparently conflicting evidence is quoted. The explanation seems to be simply that alternative mechanisms are both possible and actually used by Nature. For example, the NO method indicates that radical-chain mechanisms occur simultaneously with direct molecular reactions free from chains. As one goes up the homologous series of the paraffins the proportion of chain reaction seems to drop; and with hexane, for example, is apparently small. The only escape from this conclusion would be if there existed two kinds of chain, one sensitive to nitric oxide and the other immune. So far we have not been able to see how this could be.

The experiments of Staveley, and later of Hobbs, referred to the very initial stages of the C_2H_6 decomposition, and are not in conflict in any way with the result of Travers that in secondary processes products of higher molecular weight appear and that these secondary processes are not

* On the five preceding papers.

inhibited by NO. In view of the fact that radical and molecular reactions may all play their part, is there any difficulty in supposing that these secondary processes are predominantly molecular in nature?

Dr. G. R. Schultze (*Berlin*), said: There appears to be some difference in view-point as to whether thermochemical reactions of hydrocarbons are homogeneous in nature or influenced by surface catalysis. In this connection may I refer to an investigation we have carried out on the decomposition of normal and isobutane,¹ using as a reaction vessel a silica tube in a flow system. A monomolecular, first order reaction accounts best for the results obtained. The reactions are independent of surface influences inasmuch as nitrogen may be added up to ten times the amount of hydrocarbon without exerting any influence on the reaction velocity. If, however, the total gas pressure is reduced the reaction velocity drops off noticeably at pressures as high as 500 mm. of pure butane. This decrease may be accounted for on the basis of Lindemann's theory, although an influence of the collision factor at pressures as high as this may be somewhat unusual.

Since in the course of this discussion it was suggested that certain primary reactions may be inhibited by NO while some secondary reactions remain unaffected, it is deemed important to have some means of deciding between primary and secondary reactions. In the work mentioned before a method was used which to our knowledge was first applied by Frolich and Schneider² in hydrocarbon research. One may reproduce the results by plotting as x -axis and y -axis, respectively, the contact time or, better yet, the reaction depth as a function of the products in either total percentage of gas reacted or per cent. decomposed. The former plot shows all curves converging towards the origin. In the latter plot only those curves belonging to secondary products will start at the origin while primary products may be extrapolated to some finite value of the ordinate.

A closer inspection of the individual curves of products as to their dependence upon temperature, contact time, pressure and concentration shows that there are influences which must be explained by interaction of free radicals and there even might be a minor influence of the wall. This suggests that, at least for some individual cases, radicals and rearrangements, gas phase and surface reactions are simultaneously involved, whereby any decision in one or the other direction must be rather one of degree than of kind.

Dr. L. Küchler (*Göttingen*) said: I want to make some remarks about the influence of nitric oxide and of surfaces on the decomposition of ethane:

(1) Evidence for chains is given not only by the inhibition of C_2H_6 decomposition by NO, but also by the dependence of the rate of decomposition on the material and dimensions of the reaction vessel at pressures lower than 200 mm., as shown in Figs. 1 and 2.³

While the rate of decomposition at small pressures is larger in a glass vessel than in silica, it decreases rapidly on increasing the surface of the vessel. The difference between glass and quartz may be explained either by catalysis of the reaction by glass or by a greater effectiveness of the silica surface as chain-breaker. The retardation in a packed glass vessel can only be explained by a breaking of the chains. Here I emphasise specially that at high pressures there is no noticeable influence of the surface.

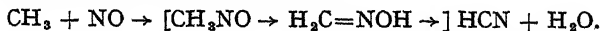
(2) It has been impossible to derive from the products detected up to the present a simple scheme for the reaction between NO and a radical. We have shown recently that HCN is produced, when C_2H_6 decomposes, in the presence of amounts of NO just sufficient to effect maximum inhibition. Quite obviously this very stable product may be the result of a complicated series of changes, but it is also possible that there is a very

¹ *Oel und Kohle*, 1938, 14, 998.

² *Ind. Eng. Chem.*, 1931, 23, 1405.

³ L. Küchler and H. Theile, *Z. physik. Chem.*, B, 1939, 42, 359.

simple reaction, starting with the direct union of the CH_3 radical and the NO and finally yielding HCN and water :



(3) Hobbs and Hinshelwood concluded from the curves for the decomposition of ethane with various pressures of nitric oxide (see Fig. 2

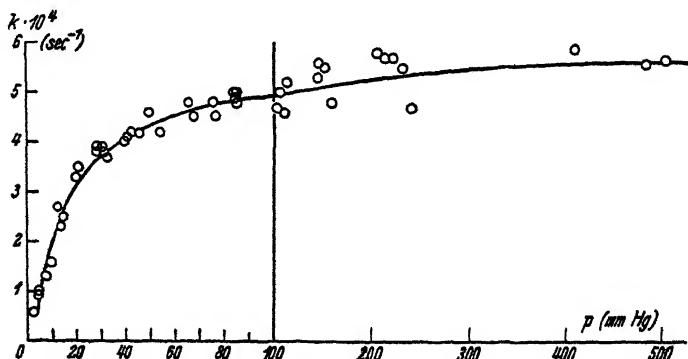


FIG. 1.—Decomposition of ethane. Variation of the first order reaction constant with pressure in silica vessel (3 l.), 883°K .

in his paper) that there is a ternary process in the normal chain-ending mechanism predominating at higher pressures. If this were so, one must expect that foreign gases would retard the rate of decomposition at higher pressures, by favouring the chain-ending. We have recently studied the action of seven foreign gases on the decomposition of C_2H_6 in the pressure range in which the first order rates are falling off.¹ We find the remarkable

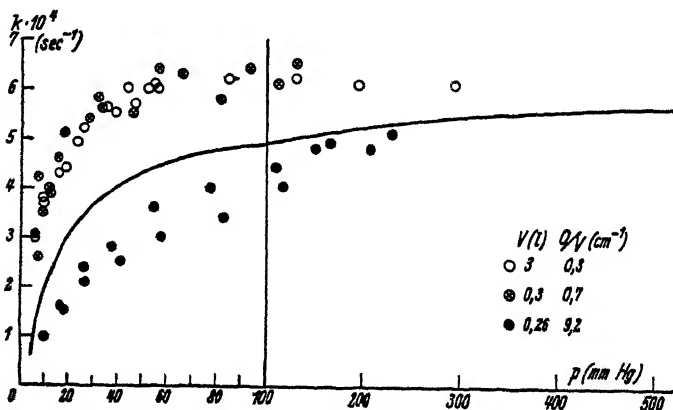


FIG. 2.—Decomposition of ethane. Variation of the first order reaction constant with pressure in various supramaxglas-vessels compared with the results obtained in silica vessel (solid curve), 883°K .

result that the first order rates calculated from the partial pressure of the ethane are appreciably higher than those obtained with pure C_2H_6 at the same pressure, even in the pressure range, at which the rates are nearly constant. Theile has now extended our experiments up to pressures of 8 atm. The silica reaction bulb had a volume of 3 l., so that wall effects must be negligible. At pressures above 400 mm. ethane the first order rates were constant within the experimental error in the case of pure

ethane and in the case of a mixture $\text{CO}_2\text{—C}_2\text{H}_6$ (5 : 1), but the latter were greater by about 60 per cent. Since this is the case, a retardation effected by radical recombination in ternary collisions with the foreign gas might be overcompensated by some sort of catalytic action of the foreign gases, so that no definite conclusion can be drawn about the mechanism of chain-breaking. In any case an alteration of the chain-ending mechanism with varying pressure seems very improbable, in view of this result. Moreover, there must be, at any rate, some uncertainty in the quantitative evaluation of the experiments with NO, especially at lower pressures, with respect to wall effects. We also studied the dependence of the mean chain length on pressure in reaction vessels of various materials and dimensions. *Absurd* results obtained in some cases have convinced us that at least in the low pressure range the maximum inhibited reaction cannot be quite identical with the homogeneous chain-free decomposition of ethane.

Dr. E. W. R. Steacie (*Montreal*), (*communicated*): One of the fundamental differences between the results of Travers and those of other workers is the much greater importance of surface effects in his investigations. In this connection it should be noted that it is a common observation that the first few runs in a new quartz or glass bulb are faster than the succeeding ones, *i.e.*, a clean surface catalyses the reactions, whereas an aged surface does not do so. By Travers' "quenching" technique the surfaces are always "clean," and hence in his investigations wall effects are of importance, although they are relatively unimportant in the work of others. It may therefore be concluded that although Travers' results give much information on the behaviour of fresh glass or quartz surfaces as catalysts, they do not, in general, furnish much information about the primary *homogeneous* decomposition reactions of the paraffins. His results are not, therefore, comparable with those of other workers.

In reply to Dr. Schultze: In our work on the decomposition of *n*- and *iso*-butane⁴ we have also noted the pronounced falling-off in rate as the pressure is lowered. This occurs at much too high a pressure to be accounted for in the case of molecules as complex as the butanes. The falling-off, therefore, appears to be due to the operation of some sort of chain mechanism.

In reply to Dr. Küchler: Recently published work⁵ has led us to the conclusion that in the case of the butane decomposition maximum inhibition by nitric oxide does not correspond to the complete suppression of chain processes.

Prof. M. W. Travers (*Bristol*), in reply, said: I am not satisfied that sufficiently definite criteria of homogeneity of gas reactions have been established, and I believe that it is often the case that the effect of surface has only been stabilised when it is supposed to be eliminated. The presence of oxygen on the surface has a very marked influence on the rate of thermal decomposition of ethane, and oxygen seems to penetrate the walls of this silical bulb. Using thick-walled silica bulbs, and preheating when filled with hydrogen, gives the most satisfactory results, but even then the difference between the results of individual experiments is greater than the experimental effort. The effect of hydrogen itself on the surface cannot be investigated in the case of ethane, but it may be large, as in the case of dimethyl ether, in which the rate of the primary change diminished in proportion to the hydrogen concentration.

What I may term the secondary decomposition of hydrocarbons is a subject, the quantitative study of which is being neglected.

With reference to Steacie's remarks, I must point out that while we hold that the primary decomposition of simple paraffin, such as ethane and propane, is influenced by surface, a view which is supported by others, we have been at some pains to point out that the formation of methane

⁴ Steacie and Puddington, *Can. J. Research*, B, 1938, 16, 176, 260.

⁵ Steacie and Folkins, *ibid.*, 1939, 17, 105.

and condensation products is a purely homogeneous process. We now show that this secondary process is uninfluenced by the presence of nitric oxide. The analytical data show that this process, which we refer to as secondary, is of importance equal to that of the primary process, in which we are not directly interested. No one else has attempted to investigate it, so there are no results with which ours are comparable.

Dr. L. A. K. Staveley (*Oxford*) said: Our experimental study of the effect of NO on the rate of decomposition of C_2H_6 and other paraffin hydrocarbons⁶ was deliberately restricted to the very early stages of the reaction, in order to avoid the complications caused by the secondary reactions which occur when the primary decomposition products accumulate. The initial reaction rates were obtained by extrapolating the almost linear pressure increase-time curves for the first two or three per cent. of the decomposition, and we believe that, for C_2H_6 , they give a true measure of the rate of production of C_2H_4 and H_2 .

Experiments with C_2H_6 , C_3H_8 , and C_6H_{14} in packed reaction vessels showed that the rates of the uninhibited decompositions are slightly reduced by a tenfold increase in the surface/volume ratio, while those of the fully inhibited reactions are somewhat increased, especially at lower pressures. The mean chain length is therefore less in a packed than in an unpacked bulb, although for ethane the difference is negligible at pressures higher than 500 mm.

In these reactions the nitric oxide is only slowly used up, and has not completely disappeared by the time the rate of pressure increase has become almost zero.

⁶ Staveley, *Proc. Roy. Soc., A*, 1937, 162, 557; Hobbs and Hinshelwood, *ibid.*, 1938, 167, 439, 447.

HOMOGENOUS THERMAL DECOMPOSITION OF SOME CYCLIC HYDROCARBONS.

BY L. KÜCHLER.

Received 27th February, 1939.

The thermal reactions of cycloparaffins and cyclo-olefins have been much less studied than those of paraffins. Yet the former are almost equally interesting and present fewer difficulties with regard to mechanism, as has been pointed out in our investigation of the thermal decomposition of dioxan.¹ For instance there is only one possibility for the primary C—C—scission in the case of cyclohexane, whereas in the case of *n*-hexane there are three.

This report deals with some investigations into the decomposition of cyclohexane, cyclohexene and methylcyclopentane. These experiments are based on a detailed investigation of the decomposition of cyclohexane, and it has proved useful also to deal with those substances which may be possible as intermediate products. This furnishes a wider base for the discussion of the mechanism of decomposition.

We are not satisfied with more or less vague estimates of the velocity of over-all decomposition and its dependence on temperature, but we also want information as to the mechanism of reaction. In this connection special importance attaches to detailed analytical investigations supple-

¹ L. Küchler and J. D. Lambert, *Z. physik. Chem., B*, 1937, 37, 285.

menting the measurements of pressure in static experiments. With regard to many rapid secondary reactions it is very important to carry out analyses after short contact times; in order to be able to analyse the products of *static* experiments with *small* conversion, we need a micro method allowing quantitative analysis of mixtures of several low-boiling hydrocarbons in very small samples. We have recently developed such a method.²

Saturated and unsaturated hydrocarbons containing two to four C-atoms are separated by adsorption on activated charcoal and subsequent fractional desorption, the activated charcoal which is placed in a capillary tube (*ca.* 20 cm. long and about 2 mm. in diameter) being first contained in a bath of solid carbon dioxide-methyl alcohol and then drawn slowly (over about 40 min.) into an electrically heated furnace (250° C.). The separate fractions are condensed in different receivers with liquid air. They contain only 1 or 2 hydrocarbons and may now be identified, *e.g.*, by burning on glowing platinum wire after a measured amount of oxygen has been admixed. Hydrogen and methane, which are the residual gases after the other gases have been condensed, are analysed by burning in the same way. This method requires for a quantitative analysis of any mixture of low boiling hydrocarbons only 1-2 c.c. gas (room temperature and 760 mm. Hg), the accuracy being about 1 per cent.

Now, in general, we fix the primary products by such analyses at different stages of reaction and by extrapolating to zero conversion. It remains to decide, whether the primary products originate from one simple reaction, or from a chain mechanism involving free radicals, as in the case of the lower paraffins.³ The inhibition of a decomposition by small amounts of nitric oxide, first observed by Staveley and Hinshelwood,⁴ seems to be specific for chain reactions involving free radicals. At any rate it is the only way in which, up to the present, we can ascertain the existence of radical chain reactions in those thermal decompositions, the investigation of which is not supported by an analogous photo decomposition. It must, however, be admitted that this method is not quite satisfactory, until more light has been thrown on the way in which nitric oxide acts.

Cyclohexene.

The decomposition of cyclohexene was studied at temperatures between 758 and 838° K. and at pressures below 200 mm. Hg.⁵

The rate calculated only from measurements of pressure is almost exactly first order over the whole course of the reaction (see Fig. 1), though analyses show that the primary products undergo rapid secondary conversions. This proves that secondary reactions cause practically no pressure change, that consequently the kinetics of the decomposition may be studied by pressure readings alone, and that conclusions so obtained are equally valid for the primary splitting up of cyclohexene.

The final pressure increase is practically equal to the initial pressure, indicating a simple fission of cyclohexene into two molecules. Analysis of the products, especially after short contact times (Fig. 2) shows, that at least for 80-90 per cent. of the primary reaction the reaction is:



² L. Küchler and O. G. Weller, *Mikrochemie* 1939, **26**, 44.

³ See *e.g.*, L. Küchler and H. Theile, *Z. physik. Chem., B*, 1939, **42**, 359.

⁴ L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 1937, 1568.

⁵ L. Küchler, *Nachr. Ges. Wiss. Göttingen* III, N.F., 1939, **1**, 231.

Here, we emphasise specially the remarkable result, that only a negligible quantity, if any, of benzene is produced in the homogenous decomposition

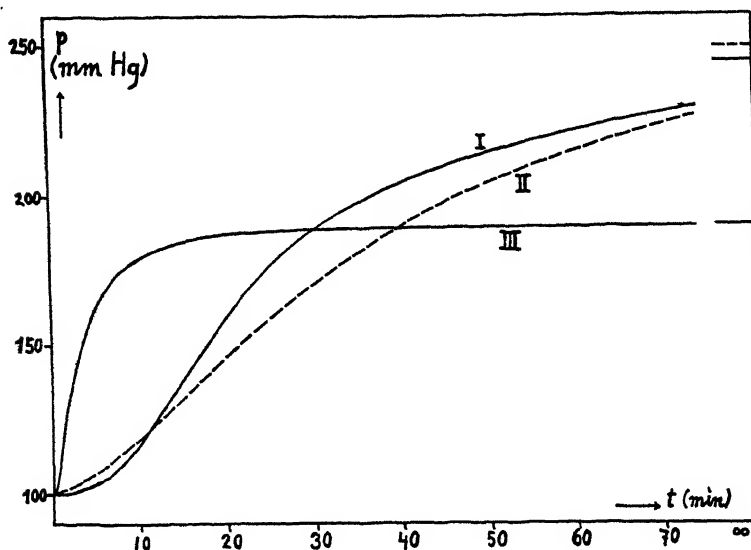


FIG. 1.—Pressure change in the decomposition of cyclohexane (I), methylcyclopentane (II), and cyclohexene (III); all 820° abs.

of cyclohexene. Therefore, in the absence of any catalyst, the 6-membered ring is split up more readily than it is dehydrogenated, whether it already contains a double bond or not.

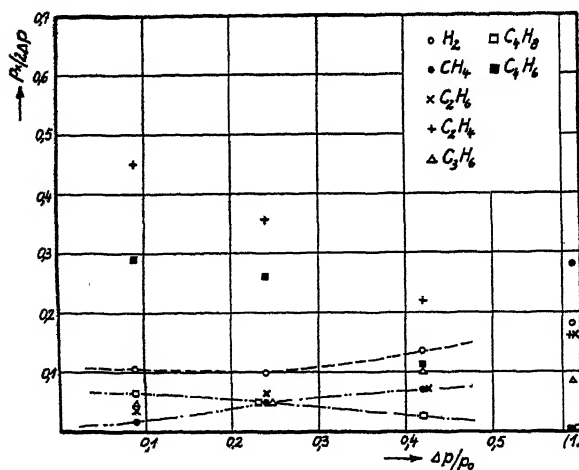


FIG. 2.—Products from cyclohexene at different stages of decomposition.

The first order rates obtained by pressure readings are constant ones, the whole pressure range down to initial pressures of 10 mm. Hg. The dependence on temperature is given by the formula

$$\log k = 12.95 - 57500/2.3 RT \text{ (sec.)} \quad (1)$$

The reaction rate is the same one in the empty (surface to volume ratio 0.8 cm.⁻¹) and in the packed (9.2 cm.⁻¹) reaction vessel (Supremaxglas); this shows the homogenous character of the decomposition.

Addition of hydrogen in equal amounts does not influence either the rate or the final pressure increase. It is only in larger quantities that hydrogen reduce the latter to any considerable extent (Table I).

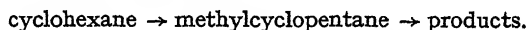
TABLE I.—THE DECOMPOSITION OF CYCLOHEXANE IN PRESENCE OF HYDROGEN.

Run.	<i>T</i> (abs.).	<i>p</i> ₀ (mm. Hg).	<i>p</i> _{H₂} (mm. Hg).	<i>p</i> _∞ / <i>p</i> ₀ .	<i>k</i> · 10 ⁴ (sec. ⁻¹).	<i>k</i> · 10 ⁴ corr. for 780° (sec. ⁻¹).
106	780	77	—	1.92	7.1	7.1
117	782 ₅	71	116	1.72	8.8	7.9
118	781 ₅	50 ₅	50 ₅	1.86	7.5	7.1
79	780	49 ₅	—	1.93	6.5	6.5
120	781	42	73	1.78	8.0	7.6
127	783	20 ₃	25 ₇	1.97	7.8	6.8

In the same way nitric oxide shows neither inhibition in small amounts nor any considerable catalysis in larger amounts (up to 75 per cent. of cyclohexene). Therefore, no radical chain mechanism seems to be involved in the decomposition of cyclohexene.

Cyclohexane.*

In the same conditions of temperature and pressure cyclohexane decomposes much more slowly than cyclohexene (compare Fig. 1). The ratio of final to initial pressure in static experiments is about 2.4. Under small initial pressure (< 50 mm. Hg) this ratio is slightly higher (2.5 — 2.6), under larger initial pressure (above 100 mm. Hg) somewhat smaller (2.3). The pressure-time curve shows at the start of the reaction a well-marked period of negligible pressure change, which has still to be dealt with. Pease and Morton,⁶ who first observed this phenomenon, assumed an isomerisation to methyl cyclopentane:



In order to test this assumption we investigated first the decomposition of pure methyl cyclopentane and secondly, this time analytically, the formation of methyl cyclopentane during the decomposition of cyclohexane. Our results do not confirm the assumption of Pease: firstly, methyl cyclopentane itself shows a lag in the pressure-time curve at the start of the reaction, though less marked than cyclohexane, and, more important, it is not produced to any remarkable amount during the decomposition of cyclohexane.

The quantitative analysis of mixtures of liquid hydrocarbons—which are not easily separated in any other way—is best effected by an investigation of the Raman spectrum.⁷ Samples of cyclohexane which had been passed through a flow apparatus were analysed in this way. Only one of such samples showed (two very faint) lines of methyl-cyclopentane, and this had been given a long contact time. After short contact time no trace of any line not belonging to the spectrum of cyclohexane was to be found. As in a mixture of as little as 2 per cent. of methyl cyclopentane in cyclo-hexane the strong lines of the former can be seen beyond doubt,

* In part these investigations were carried out by assistance of Mr. O. G. Weller

⁶ R. N. Pease and J. M. Morton, *J. Amer. Chem. Soc.*, 1933, **55**, 3190.

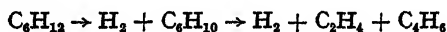
⁷ See, e.g., J. Goubeau, *Z. angew. Chem.*, 1938, **51**, 11. For these analyses I am much indebted to Dr. Goubeau and Herr Thaler.

we may be sure that in those samples there is no more than 1 per cent. of methyl-cyclopentane. If Pease's assumption were correct we should have found about 30 per cent., considering the temperature and contact time applied. This means that not even 10 per cent. of the cyclohexane decompose by isomerisation to methylcyclopentane.

TABLE II.—PRODUCTS FROM CYCLOHEXANE.

Temp. (abs.).	909 (Flow).		812 (Static).	
	2 sec.	7.5 sec.	6 min.	12 min.
Contact Time				
Gaseous Products (Mol. per cent. of introd. C_6H_{12}) .	0.6	4.0	6	25
H_2 (Mols. per 100 mols. gaseous products) . .	28	24	21.5	17.5
CH_4	4.5	4.5	7	11.5
C_2H_4	17	19	71.5	15
C_2H_6	7	8.5		12.5
C_3H_8	18.5	17.5		23.5
C_4H_8	17	18.5		14.5
C_4H_{10}	8	8		4.5

The analysis of gaseous products from cyclohexane up to very small conversion is shown by Table II.* The percentage of hydrogen is larger in the experiments with small conversion; this shows the following simple reaction mechanism:



For two reasons, however, this cannot be the only way of the decomposition:

(1) The ratio of p_∞/p_0 ought to be about 3 (at least 2.8) but not 2.4 (see the experiments on the decomposition of cyclohexene with addition of hydrogen).

(2) The presence of a comparatively large amount of propene in the experiment with the shortest contact time could not be explained.

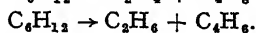
We must therefore assume that cyclohexane splits up also into two molecules: especially into two molecules of propene



The two following reactions cannot, however, be altogether disregarded on the ground of our analyses:



and



The first order is valid for the pressure change in the course of an experiment with the exception of the beginning. The dependence of maximum rate of pressure increase—we take here $\left(\frac{dp}{dt}\right)_{\max.}$ instead of $\left(\frac{dp}{dt}\right)_0$ —on initial pressure follows best the $3/2$ power in the pressure range from 10 to 200 mm. Hg:

$$\left(\frac{dp}{dt}\right)_{\max.} = k p_0^{3/2} \quad . \quad . \quad . \quad (2)$$

* We have only analysed the gaseous products but a comparison of the number of mols. found and to be expected from pressure increase shows that higher hydrocarbons are not produced to any larger extent.

The dependence on temperature of k is given by the formula :

$$\log k = 11.7 - 13,000/T \text{ (mm. Hg and sec.)}. \quad (3)$$

The rate of decomposition has been found equal in packed reaction vessels, though some experiments showed rates about 15 per cent. lower. Hydrogen, if not in too great surplus, has no influence on the reaction velocity.

The period of negligible pressure change at the start of the reaction is of special interest. It has already been mentioned that Pease and Morton's explanation is not correct. It can readily be seen by analyses, that it is, in fact, a matter of inhibition of the decomposition but not of close balance between a dissociation and a polymerisation. The most obvious explanation would be that cyclohexane decomposes in a chain mechanism, which is inhibited by small amounts of impurities until these impurities are consumed. This, however, is opposed by the fact, that nitric oxide has no influence on the velocity of decomposition (Table III) and on the lag of the pressure time curve.

TABLE III.—EFFECT OF NO ON THE DECOMPOSITION OF CYCLOHEXANE.

Run.	T (abs.).	p_0 (mm. Hg.).	p_{NO} .	p_{∞}/p_0 .	$\left(\frac{dp}{dt}\right)_{\max.}$ (mm. Hg./min.)
19	813	76	—	2.32	2.30
7	813	83	7	2.49	2.53
8	813	89	3	2.38	3.00
4	813	95	—	2.34	3.66
11	813	100	98	—	4.40
2	813	100	—	2.32	3.75
12	813	101	—	2.41	3.85
10	813	106	2.5	—	3.95
9	813	108	23.5	2.40	3.53

Apart from this, it is a remarkable fact that the retardation is specially marked when the reaction vessel has, before the experiment, been well pumped out for a long time while being heated. On the other hand, the induction period is notably diminished by small amounts of reaction products (this is done already by insufficient pumping out between two experiments). But it does not entirely disappear even when larger quantities of products are present.

In this case two phenomena must be clearly distinguished. An S-shaped pressure-time curve has always to be expected in those cases where a secondary dissociation of primary products takes place, and, moreover, its rate of dissociation is greater than that of the primary decomposition. In the decomposition of cyclohexene, too, the initial rate—just at the start of the reaction—is 20 to 25 per cent. smaller than would correspond to the later course of the reaction. In the case of cyclohexane, where the final pressure increase is more than 100 per cent. this effect is consequently stronger. In the case of cyclohexane, moreover, there is also an initial inhibition of the primary decomposition; apparently, pure cyclohexane decomposes only with great difficulty. I cannot as yet formulate a precise explanation for this interesting fact, but quite probably, an inhibition of energy transfer may account for it. The results of sound dispersion measurements showed that such an inhibition is usually very high in the case of pure gases.⁸ In any case, this induction period seems to be very interesting for future investigations.

Methylcyclopentane.

The decomposition of methylcyclopentane is very similar to that of cyclohexane. Here, too, we observe a strong inhibition at the beginning of the reaction. The final pressure increase amounts, as in the case of

⁸ See e.g., A. Eucken and L. Küchler, *Z. techn. Physik*, 1938, 19, 517.

cyclohexane, to about 150 per cent. of the initial pressure. The dependence of the maximum pressure increase on the initial pressure also corresponds to a higher order than the first. The dependence on temperature is given by the following formula—corresponding to equation (3):

$$\log k = 11.5 - 13,000/T \quad (4)$$

It must however, be pointed out that, over the whole pressure range (10-150 mm. Hg), the maximum pressure increase is better reproduced by the power 1.3.

In the gaseous products there are more propene and less C_4 —hydrocarbons as compared to the products of cyclohexane. But detailed analyses are still missing.

Summary.

Investigations are reported dealing with the thermal decomposition of cyclohexane, cyclohexene, and methyl-cyclopentane. Cyclohexene decomposes in the neighbourhood of $800^\circ K$ in a first-order reaction, the primary products being ethylene and butadiene. Cyclohexane primarily decomposes in part to cyclohexene and hydrogen, in part by opening the ring yielding two molecules of propene. There is no isomerisation to methyl-cyclopentane in any appreciable amount. Methyl-cyclopentane also shows a period of negligible pressure change in the beginning of the reaction, as cyclohexane does.

*Göttingen, Institut für physikalische Chemie
der Universität.*

THE EXISTENCE OF METHYLENE IN HYDROCARBON REACTIONS.

BY R. F. BARROW, T. G. PEARSON, AND R. H. PURCELL.

Received 21st March, 1939.

1. The object of this paper is to draw together and summarise as far as possible the present state of our knowledge concerning the methylene radical. Its presence as an intermediate has been frequently postulated to account for the analytic and kinetic data concerning the decomposition,¹ oxidation,² and polymerisation *e.g.*³ of hydrocarbons, but actual proof of its presence has afforded unexpected difficulties, and its existence as an intermediate substance in such reactions is not yet generally accepted. It seems worth while, therefore, to detail the evidence in the hope that this will serve to clarify the present position.

2. The first direct evidence for the existence of methylene was adduced by Norrish, Crone and Saltmarsh,⁴ who measured the wavelengths of the diffuse bands in the absorption spectrum of keten, observed that the region most responsible for photo-dissociation corresponded with the absorption region of the carbonyl group, and found that dissociation was accompanied by the formation of ethylene and carbon

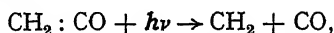
¹ Kassel, *J.A.C.S.*, 1932, **54**, 3949.

² Norrish, *Proc. Roy. Soc., A*, 1935, **150**, 36.

³ *Trans. Faraday Soc.*, 1936, **32**, 1.

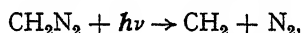
⁴ Norrish, Crone, Saltmarsh, *J.C.S.*, 1933, 1533.

monoxide in the molecular ratio 1 : 2. These results led the authors to conclude that: (1) "The primary change is simply interpreted as a splitting of the molecule at the olefinic bond according to the equation



the liberated CH_2 reacting further with undecomposed keten, to give ethylene and carbon monoxide: $\text{CH}_2 : \text{CO} + \text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{CO}.$ " (2) "The energy relationships from the primary change when analysed, show that it cannot be represented purely as a rupture of the olefinic bond; they are, however, consistent with a decomposition into CH_2 and CO molecules, each containing carbon in the bivalent form." This deduction was made in order to reconcile the spectroscopic data with the known heats of formation, the minimum quantum effecting decomposition corresponding with $\lambda = 3850 \text{ \AA}.$, or 74 kg.-cal. per mol., the maximum with 2600 $\text{\AA}.$, or 110 kg.-cal. per mol., neither of which is comparable with the 167 kg.-cal. necessary for the rupture of the olefinic bond in the ordinary way to yield CO and CH_2 radicals. Ross and Kistiakowsky⁵ repeated and confirmed these experiments and determined in addition the overall quantum yield of the reaction.

A study of the photochemical decomposition of diazomethane by Norrish and Kirkbride⁶ showed that in this case also the results could be explained by postulating that the primary act of dissociation yields a methylene containing carbon in the bivalent condition,



which is followed by a short chain of secondary reactions, consuming about four molecules of diazomethane.

The formation of methylene during the photodissociation of keten and diazomethane was subsequently confirmed by Pearson, Purcell, and Saigh,⁷ who allowed these compounds to stream at a low pressure along a quartz tube irradiated over a short length by the light from a mercury vapour arc. The methylene radicals formed passed along the tube where they were identified by their reactions with selenium and tellurium to give seleno- and telluro-formaldehydes respectively. Meanwhile, Rice and Glasebrook⁸ had obtained methylene by the thermal decomposition of diazomethane, and this was confirmed by Pearson, Purcell and Saigh. The life-period of methylene in the presence of excess of diazomethane, but in the absence of a carrier gas, was found to be 5.0×10^{-3} sec. when produced thermally, and 6.4×10^{-3} sec. when produced photochemically, values which were held to be identical within the limits imposed by the experimental methods. The methylene formed by the photodissociation of keten, in the presence of an excess of this gas, showed no diminution in concentration in passing along 80 cm. of 11 mm. diameter quartz tubing during 0.05 sec., in which time each radical must have made 3×10^3 impacts with the wall of the tube, and 4×10^5 impacts with other molecules. The half-value period of methylene prepared from, and in the presence of, diazomethane, was extended to 0.2 sec. by dilution with keten, or with other inert gases such as ether or nitrogen, by the suppression of a bimolecular reaction between diazomethane and methylene which probably occurred on the walls of the

⁵ Ross and Kistiakowsky, *J.A.C.S.*, 1934, **56**, 112.

⁶ Norrish and Kirkbride, *J.C.S.*, 1933, 119.

⁷ Pearson, Purcell, and Saigh, *ibid.*, 1938, 409.

⁸ Rice and Glasebrook, *J.A.C.S.*, 1934, **56**, 2381.

reaction tube. Although Rice and Glasebrook⁸ had produced what appeared to be excellent evidence of the existence of methylene in the thermal decomposition of diazomethane, Rice⁹ later brought forward, in a preliminary communication, certain evidence which cast doubt on the conclusions he had drawn. In the absence of a more detailed publication, and in view of Pearson, Purcell, and Saigh's findings, we are compelled to accept as valid his earlier work, which is in accord with the remainder of the experimental results.

3. Spectroscopic evidence for the existence of methylene is meagre, and, largely owing to the very low intrinsic luminosity of many of the sources investigated, band-head data are very inadequate. Mecke¹⁰ has reported weak and very diffuse bands in the region 4370-4020 Å., occurring in the absorption spectrum of the products of thermal decomposition of methane at 800-900° C., and suggested that these bands may be due to CH₂. At least two other distinct band systems, associated with hydrocarbon reactions, are reported in the literature, being grouped together somewhat misleadingly under the heading of "ethylene-flame bands." Emeléus¹¹ using the phosphorescent flame of ether, Rassweiler and Withrow¹² in a spectroscopic study of the ordinary Bunsen flame, and Ubbelohde¹³ in the chemi-luminescent combustion of hydrocarbons, have reported band-systems which are held provisionally by the present authors, to be identical. Fowler and Pearse (*vide* Ubbelohde,¹³) have shown the emitter of these bands to be activated formaldehyde by comparison of Emeléus' and Ubbelohde's photographs with those of Gradstein¹⁴ of the fluorescent spectrum of formaldehyde. Bell¹⁵ observed in the emission spectrum of methane-air-nitrogen mixtures a similar system of bands which he identified with those of Vaidya (see below), ascribing them to the methylene radical. A mere comparison of wavelength data is insufficient, however, to establish the identity of Bell's bands with either those of Emeléus or of Vaidya.

Vaidya¹⁶ describes an extensive system of bands, at 2500-4100 Å., occurring in the flame of ethylene burning in air. Vibrational analysis of these bands revealed frequencies of vibration of the orders 1880 cm.⁻¹ and 1070 cm.⁻¹. The latter may perhaps be identified with the valence vibration of the C—O link, while the group responsible for the larger frequency is uncertain. The provisional identification of the C—O link, and the fact that the emitter of the bands of Emeléus *et al.* has been shown to be due to the formaldehyde molecule, perhaps lends weight to Vaidya's suggestion that the emitter of his bands is the CHO radical. Additional evidence for this view may be adduced from studies of the dissociation of formaldehyde, which is known to be present under the conditions of Vaidya's experiments. From the analysis of the ultra-violet absorption spectrum of formaldehyde, previously investigated by Henri and Schou,¹⁷ Herzberg¹⁸ has indicated that the dissociation by

⁸ Rice, *Chem. Reviews*, 1935, 17, 60.

¹⁰ Mecke, *Trans. Faraday Soc.*, 1934, 30, 176.

¹¹ Emeléus, *J.C.S.*, 1926, 2948.

¹² Rassweiler and Withrow, *Ind. Eng. Chem.*, 1932, 24, 529.

¹³ Ubbelohde, *Proc. Roy. Soc., A*, 1935, 152, 354.

¹⁴ Gradstein, *Z. physikal. Chem., B*, 1933, 22, 384.

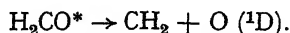
¹⁵ Bell, *Proc. Roy. Soc., A*, 1937, 158, 429.

¹⁶ Vaidya, *ibid.*, 1934, 147, 513.

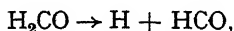
¹⁷ Henri and Schou, *Z. Physik*, 1928, 49, 774.

¹⁸ Herzberg, *Trans. Faraday Soc.*, 1931, 27, 378.

increasing the vibrational energy in the upper state of these bands may be represented by

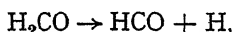


The total amount of energy for this dissociation from the ground state is found to be 195 kg.cal./mol., corresponding to the thermal data for the energy of dissociation into CH_2 and O, both in the ground states, of 155 kg.cal./mol., plus the energy absorption of the transition, $\text{O} (^3P) \rightarrow \text{O} (^1D)$, of about 45 cal. The beginning of predissociation of formaldehyde (ca. 2750 Å.) gives an upper limit to the dissociation energy of the normal molecule: Herzberg found this to be 105 kg.cal. per mol., corresponding probably to

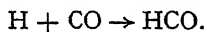


a mechanism analogous to that proposed for the dissociation of phosgene by Bodenstein.¹⁹

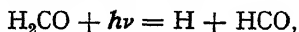
There appears to be no fundamental objection to be urged against the dissociation of formaldehyde in its ground state, as postulated by Herzberg and by Henri²⁰ into HCO and H, although it may seem superficially to conflict with the chemical evidence of Norrish,²¹ that the primary dissociation products are carbon monoxide and hydrogen. Of the two mechanisms proposed by Löcker and Patat,²² the present authors are inclined to accept the primary dissociation,



followed by interaction of the hydrogen atom with the HCO residue, to give carbon monoxide and molecular hydrogen. Mecke²³ has shown that the dissociation of the HCO radical is practically thermo-neutral, while Frankenburger²⁴ has indicated in his study of the action of hydrogen atoms on carbon monoxide, that the primary process is a direct combination,



That HCO radicals have a sufficiently long life-period in Frankenburger's²⁵ experiments to allow of the formation of considerable quantities of glyoxal, while in the decomposition of formaldehyde, no glyoxal is formed, may reasonably be ascribed to differing experimental conditions. In agreement with this are the experiments of Gorin,²⁶ who studied the photolysis of acetaldehyde and formaldehyde in presence of iodine. In the first case he found that the formation of hydrogen iodide begins to take place above 100°, suggesting the decomposition of formyl radicals at this temperature. He gives an upper limit for the activation energy of the dissociation of 26 kg.cal./per mol. The photolysis of formaldehyde under the same conditions with light of wave-length shorter than 3650 Å. produced only carbon monoxide and hydrogen iodide in the molecular ratio 1 : 2, indicating the primary process:



¹⁹ Bodenstein, *Z. physikal. Chem.*, B, 1929, 3, 459.

²⁰ Henri, *Leipzig. Vortr.*, 1931, 126.

²¹ Norrish, *Trans. Faraday Soc.*, 1931, 27, 391.

²² Löcker and Patat, *Z. physikal. Chem.*, B, 1934, 27, 431.

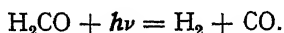
²³ Mecke, *Nature*, 1930, 125, 526.

²⁴ Frankenburger, *Z. Elektrochem.*, 1930, 36, 757.

²⁵ *Idem.*, *Trans. Faraday Soc.*, 1931, 27, 409.

²⁶ H. S. Taylor, *J. Physical Chem.*, 1938, 42, 770.

while at wave-lengths longer than 3650 Å., molecular hydrogen was also formed by the reaction,



Gorin further stated that below 100° HCO radicals do not react with iodine, but do react readily to give $\text{H}_2\text{CO} + \text{CO}$. The occurrence of this reaction may account for Burton's failure to detect hydrogen atoms arising from the decomposition of HCO radicals, and in view of this we find it difficult to accept Burton's suggestion²⁷ that HCO radicals are completely stable at 100°. The authors' view that the primary decomposition of formaldehyde results in the liberation of an HCO radical, (*cf.* Burton²⁷) which rapidly interacts with the hydrogen atom set free, is in general agreement with the views of Leighton,²⁸ and is not in conflict with the suggestion that Vaidya's bands arise by the emission of light from the same radicals.

In conclusion of this section, it does not appear that any known band-system with the possible exception of that of Mecke (*vide supra*), can be ascribed to CH_2 , for which "bent molecule" he²⁹ calculates the following normal vibration frequencies:

$$\begin{aligned}\nu(\sigma) &= 3060 \text{ cm}^{-1} \\ \nu(\pi) &= 2980 \text{ cm}^{-1} \\ \delta(\pi) &= 1450 \text{ cm}^{-1}\end{aligned}$$

In particular, the authors cannot agree with Bell that Vaidya's bands are to be more reasonably ascribed to the CH_2 group than to the CHO group.

Despite the absence of a band-system which can be identified with methylene, it is significant to notice that when methane is subjected to a glow discharge in an apparatus submerged in liquid air, it is converted quantitatively into ethylene and hydrogen. At higher temperatures the products consist of a complex mixture of saturated and unsaturated hydrocarbons (Brewer and Kueck).³⁰

4. The occurrence of methylene as an intermediate in the dissociation, polymerisation, and oxidation of hydrocarbons has long aroused considerable interest. The first attempt to establish the existence of a stable bivalent form of carbon was described by Nef.³¹ He concluded "that organic compounds readily undergo a primary decomposition into a stable smaller molecule and a radical containing bivalent carbon." Much earlier, Marchand³² had obtained large quantities of methane during the decomposition of ethylene at bright red heat, and concluded that the ultimate resolution of a hydrocarbon into its elements at high temperatures cannot be regarded as the result of a single chemical change. These views were clarified by Bone and Coward³³ in an investigation of the decomposition of methane, ethane, ethylene and acetylene between 500° and 1200°. An examination of the residues revealed the existence of intermediate stages, and the authors supposed that the primary effect, in the cases of ethane and ethylene, is an elimination of

²⁷ Burton, *J.A.C.S.*, 1938, **60**, 212; *J. Chem. Physics*, 1938, **6**, 818.

²⁸ Leighton, *J. Physical Chem.*, 1938, **42**, 760.

²⁹ Mecke, *Leipzig. Vortr.*, 1931, 46.

³⁰ Brewer and Kueck, *J. Physical Chem.*, 1931, **35**, 1293.

³¹ Nef, *Annalen*, 1892, **270**, 267; 1894, **280**, 291; 1895, **287**, 265; 1897, **298**, 202.

³² Marchand, *J. prakt. Chem.*, 1839, **36**, 478.

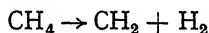
³³ Bone and Coward, *J.C.S.*, 1908, **93**, 1191.

hydrogen and the dissolution of the bond between the carbon atoms to yield residues such as $=CH_2$ and $\equiv CH$. This research was the first of a long series of investigations by Bone and his collaborators, in consequence of which he³⁴ reaffirmed his belief in the existence of the methylene radical.

In 1932 Kassel¹ studied the decomposition of methane at 700-800°, and showed that the reaction is homogeneous and kinetically of the first order. Of the two ways in which the reaction might conceivably occur, *viz.*,



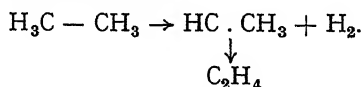
he favoured the latter on the ground of a comparison of the heats of these reactions and the experimental heat of activation, and concluded that methylene is a comparatively inert substance. This inference was in agreement with some experiments which were described by Belchetz³⁵ and Rideal.³⁶ A rapid stream of methane at 0.01 mm. pressure was allowed to pass over a strongly heated platinum or carbon filament and then to impinge on a cooled surface, covered with tellurium or iodine. When the distance from the filament to the cooled surface exceeded the mean free path of the molecules, the methyl radical alone was identified. When the distance was within the mean free path, the tellurium was attacked to yield a minute amount of material which was considered to be methylene telluride; and iodine mirrors gave methylene iodide. Atomic hydrogen was also detected. The energy of activation of the decomposition, assumed to be



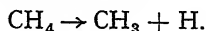
was found to be 95 kg.cal. A similar value was obtained for the activation energy of the decomposition,



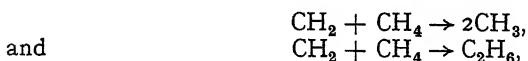
No direct evidence of the occurrence of ethylidene radicals was forthcoming. Nevertheless, this correspondence of the activation energies suggested to the authors that the mechanisms of the decompositions were analogous, requiring in the case of ethane, the removal of two hydrogen atoms from the same carbon atom:



Meanwhile Rice and Dooley³⁷ investigated the thermal decomposition of methane in a heated quartz tube. They were unable to detect methylene or atomic hydrogen but obtained large quantities of methyl and considered that the primary process was:



If, they said, the primary product were CH_2 , then the reactions:



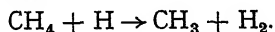
³⁴ Bone, *Trans. Faraday Soc.*, 1934, **30**, 150.

³⁵ Belchetz, *ibid.*, 1934, **30**, 170.

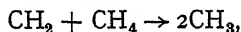
³⁶ Belchetz and Rideal, *J. Amer. Chem. Soc.*, 1935, **57**, 1168.

³⁷ Rice and Dooley, *ibid.*, 1934, **56**, 2747.

must have activation energies of less than 12 kg.cal. in order to account for the absence of methylene radicals. This, they suggested, could not be the case, for the activation energy of the reaction between methylene and ether is about 15 kg.cal. (Rice and Glasebrook).³⁸ They ascribed the disappearance of the atomic hydrogen either to a wall reaction, or to the reaction with methane, *i.e.*



While there are admittedly surprising discrepancies (see ⁷) between the experimental results recorded in Belchetz' preliminary paper,³⁵ and in his later paper with Rideal,³⁶ yet the general trend of results points to the conclusion that methylene radicals are the primary product of the dissociation of methane, and that they react readily to give methyls. The inability of Rice *et al.* to detect methylene, and of Belchetz to obtain it if his detector mirrors were situated at distances greater than that of the mean free path from the filament, becomes perfectly comprehensible if we assume that the reaction,



though slow at room temperatures, occurs readily at the higher temperatures of the experiments of the above workers.

Kassel³⁹ calculated the probable ratio of the concentrations of H and CH₃ under Rice's experimental conditions, and concluded that $(\text{H}) \gg 10^4(\text{CH}_3)$, which "conflicts hopelessly with Rice and Dooley's experiments in which methyl groups could be detected, but no atomic hydrogen," and that "the experimental kinetics of the decomposition of methane cannot be explained by any mechanism which involves free methyl radicals." Unfortunately, Rice's test for the absence of hydrogen atoms, namely, the absence of a grey ring of metallic tellurium on evaporation of the condensate in a liquid air trap due to the decomposition of hydrogen telluride, is completely untrustworthy. Hydrogen telluride is stable enough, especially in a dry apparatus, to withstand vaporisation from a glass surface which has been cooled in liquid air.

Subsequently, in a paper entitled "Attempts to prepare the methylene radical by the thermal decomposition of hydrocarbons,"⁴⁰ Rice states rather ambiguously that "using much longer wires (*cf.* Belchetz and Rideal³⁶) and larger mirrors our results agreed with those reported by Belchetz and Rideal, and were similar to those obtained by passing methane through a quartz furnace (Rice and Dooley);³⁷ dimethyl telluride was obtained and identified by its m.p. 19.5°." It is difficult to see how the results could be similar both to Belchetz' and to Rice and Dooley's. He concludes by restating his belief in the primary production of trivalent carbon, suggesting that even when divalent carbon is produced it readily passes into the trivalent form. In the absence of a detailed report of Rice's experiments, it seems to us that the fairest conclusion that can be drawn is that methylene, as well as methyl, may be one of the primary products in the dissociation of methane. Methylene radicals so formed may then undergo a rapid reaction with either methane, hydrogen, or another methylene radical, resulting in the production of methyl radicals. This cautious conclusion is dictated by our knowledge of the difficulties inherent in the unambiguous identification of products from experiments with filaments at low pressures, by the

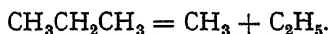
³⁸ Rice and Glasebrook, *J. Amer. Chem. Soc.*, 1934, **56**, 2381.

³⁹ Kassel, *ibid.*, 1935, **57**, 833.

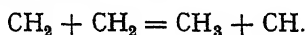
⁴⁰ Rice, *ibid.*, 1939, **61**, 213.

absence of quantitative data concerning the extent to which the dissociation of the hydrocarbon proceeds *via* a mechanism involving free radicals, and the equivocal nature of the evidence which may be adduced from kinetic experiments. The formation of ethylene (*vide e.g.* Storch),⁴¹ excepting under very special circumstances, is no proof of the primary formation of methylene, for even in the work of Paneth, Hofeditz, and Wunsch⁴² with lead tetramethyl, where methyl was undoubtedly the primary product, appreciable amounts of ethylene were formed, probably as a result of the disproportionation $\text{CH}_3 + \dot{\text{C}}\text{H}_3 = \text{CH}_2 + \text{CH}_4$, followed by $2\text{CH}_2 = \text{C}_2\text{H}_4$. The process $\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2$ does not appear to occur readily in the Schumann ultra-violet dissociation of methane.⁴³

5. Closely related to methylene is ethylidene, $\text{CH}_3 : \text{CH}$, to which, in the decomposition of higher hydrocarbons, has been ascribed a rôle similar to that played by methylene in the decomposition of methane. Belchetz and Rideal⁴⁴ found that propane decomposed on a platinum filament at 1750° with the formation of some methylene, which reacted with warm tellurium mirrors to yield telluroformaldehyde. Cold mirrors gave only dimethyl telluride and dimethyl ditelluride, presumably through the reduction of the telluroformaldehyde by other species present. Earlier Rice, Johnson, and Evering⁴⁵ had found only methyl and ethyl radicals, identified by the melting-points of their mercury bromide derivatives, which indicated that the primary act in the dissociation was :



Belchetz and Rideal were unable to detect ethyl radicals, and suggested that the ethyl mercuric bromide in Rice, Johnson, and Evering's experiments was, in fact, a fortuitous mixture of mercuric bromide with methyl mercuric bromide. This is supported by the fact that Rice and Glasebrook obtained only dimethyl ditelluride by the reaction of the radicals with tellurium. They concluded that methyl was a secondary product arising from methylene. Thus, although diazomethane yields methylene when heated to 450°, at 650° methyl, but no methylene, can be detected.^{7, 38} Evidently methylene can react with itself, or with other molecules, to yield methyl: *e.g.*



It is noteworthy that 600° corresponds with the beginning of the deposition of carbon in the heated zone, and the incidence of a chain reaction in the decomposing gas.⁷ Belchetz and Rideal concluded that the initial act in the decomposition of propane and *n*-butane is similar to that occurring in the decomposition of methane: *i.e.* the production of hydrogen and the corresponding olefin, which can then dissociate into hydrogen and the next lower olefin.

The question now arises as to whether the olefin is liberated as such, or as the isomeric free radical, homologous with methylene. The evidence here is as follows. Rice and Glasebrook⁴⁶ by decomposing diazoethane at 650° found evidence of ethylene, but none of ethylidene, in agreement

⁴¹ Storch, *J. Amer. Chem. Soc.*, 1932, **54**, 4188.

⁴² Paneth, Hofeditz, and Wunsch, *J.C.S.*, 1935, 372.

⁴³ Groth, *Z. Elektrochem.*, 1939, **45**, 271.

⁴⁴ Belchetz and Rideal, *J.A.C.S.*, 1935, **57**, 2466.

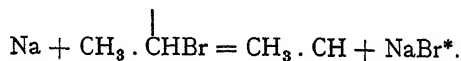
⁴⁵ Rice, Johnson, and Evering, *ibid.*, 1933, **55**, 3529.

⁴⁶ Rice and Glasebrook, *ibid.*, 1934, **56**, 2472.

with Belchetz' failure to observe it in the decomposition of the higher homologues of methane.⁴⁴ Recent experiments in these laboratories have indicated, however, that at lower temperatures, *viz.* 400-450°, diazoethane yields active fragments which combine with selenium and tellurium to yield compounds of which the properties are closely similar to those of seleno- and telluro-acetaldehydes.

Diazomethane was prepared by two independent methods: by the action of a sodium alcoholate solution on either nitrosoethylurethane according to Meerwein and Burneleit,⁴⁷ or nitrosoethylaminoketone according to Adams and Kenner.⁴⁸ In a typical experiment, diazoethane was passed through a silica tube heated over a restricted zone by means of an electric furnace to 400°. The products of the dissociation passed along the tube, and were allowed to impinge on a selenium (or tellurium) mirror at the room temperature, situated 8 cm. from the furnace mouth. The mirror was removed in seven minutes. The product of the reaction with selenium was collected in a liquid air trap. The characteristic odour of the alkyl selenides was absent. On addition of acetone solutions of the mercuric halides, the product gave precipitates possessing properties identical with those of the mercuric halides of selenoacetaldehyde. At higher furnace temperatures the yield of radicals progressively decreased, until at 600°, the attack on very thin mirrors was imperceptible even after ten minutes. Decomposition could be equally well effected by the light from a hot or a cold mercury arc, and the reactive fragments had properties identical with those produced thermally.

Finally, it is of interest to note that in the luminescent reactions of sodium vapour with ethylidene bromide investigated by Bawn and Dunning,⁴⁹ it has been suggested⁵⁰ that the luminescence arises from the reaction,



6. The evidence which has been outlined in this paper is in many ways confusing, involving as it does a number of conflicting experimental data. There is no doubt, however, that methylene has been isolated, and exists as an intermediate in numerous reactions, but there seems no experimental proof that the methylene contains bivalent carbon. As Norrish⁵¹ has already pointed out, the evidence from the photodissociation of diazomethane and keten does not establish this fact. In the former case, for example, the change $\text{CO} (^3\pi) = \text{CO} (^1\Sigma)$, provides sufficient energy to compensate for the deficiency in the light quantum responsible for the dissociation. Further, arguments based on Mecke's calculation⁵² of the energies necessary to strip the successive hydrogen atoms from methane appear to conflict with the more recent work of Voge.⁵³ Nevertheless, theory appears to show that the ground state of methylene is a singlet arising from bivalent carbon.⁵⁴ None of the experimental evidence conflicts with this, and it must therefore remain the authors' present view. But, clearly, confirmation must await the result of spectrographic investigation. The properties of ethylidene may be

⁴⁷ Meerwein and Burneleit, *Ber.*, 1928, **61**, 1840.

⁴⁸ Adams and Kenner, *J.C.S.*, 1937, 1551.

⁴⁹ Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35**, 185.

⁵⁰ Evans, *ibid.*, 193.

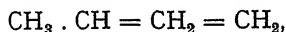
⁵¹ Norrish, *ibid.*, 191.

⁵² Mecke, *Z. Elektrochem.*, 1930, **36**, 589.

⁵³ Voge, *J. Chem. Physics*, 1936, **4**, 581.

⁵⁴ Lennard-Jones, *Trans. Faraday Soc.*, 1934, **30**, 70.

expected to be similar, but for the probability of its removal by the reaction,



to which it has been impossible to ascribe an activation energy.

In conclusion we list here some of the reactions by which methylene may be removed when in contact with hydrogen or methane:

1. $\text{CH}_2 + \text{CH}_2 = \text{C}_2\text{H}_4$
2. $\text{CH}_2 + \text{H}_2 = \text{CH}_4$
3. $\text{CH}_2 + \text{H}_2 = \text{CH}_3$
4. $\text{CH}_2 + \text{CH}_4 = 2\text{CH}_3$

Of these, 1 and 2 are strongly exothermal, require three-body collisions, and involve an uncertain steric factor. We may anticipate that both reactions are inefficient. Reactions 3 and 4 are almost thermo-neutral (for reaction 3, see Rosenblum,⁵⁵ and Jungers and Taylor),⁵⁶ and appear to require only small activation energies. From a qualitative consideration of such reactions, the rapid disappearance of methylene in systems containing hydrogen, or hydrocarbons, becomes readily comprehensible (see also, ^{57, 58}).

*Imperial College,
London, S.W. 7.*

⁵⁵ Rosenblum, *J.A.C.S.*, 1938, **60**, 2819.

⁵⁶ Jungers and Taylor, *J. Chem. Physics*, 1938, **6**, 325.

⁵⁷ Storch and Kassel, *J.A.C.S.*, 1937, **59**, 1240.

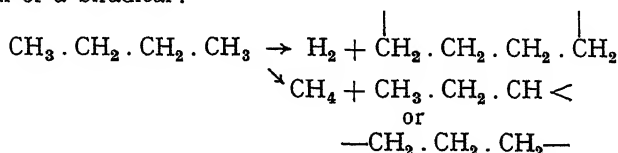
⁵⁸ Steacie, *Chem. Reviews*, 1938, **22**, 311.

THE STABILITY OF HYDROCARBON BIRADICALS AND THEIR REACTIONS.

By C. E. H. BAWN AND J. MILSTED.

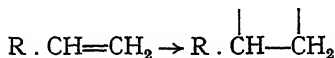
Received 21st March, 1939.

There is considerable uncertainty at the present time concerning the exact mechanism by which hydrocarbons decompose on heating. One aspect of this problem is the understanding of the rôle which free radicals play in these processes. This information can be most easily obtained by a detailed study of the stability and reactions of the elementary radicals themselves. Much progress has already been made in this respect by the use of the methods of atomic reactions and photochemistry. More recently, it has become increasingly apparent that biradicals may be the important intermediaries in thermal and photochemical decompositions and polymerisations. For instance, there is some support for the suggestion that the initial stage in the thermal decomposition of hydrocarbons is 1:2 or 1:4 loss of hydrogen or methane with the formation of a biradical:¹



¹ Kassel, *J. Chem. Physics*, 1933, **1**, 749.

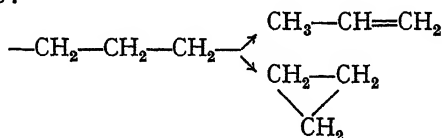
The opening of the double bond may be the primary process in the photol and thermal polymerisation of unsaturated molecules : ²



Also the recent experiments of Norrish and Bamford ³ on the photolysis of cyclic ketones indicate the formation of tetramethylene and higher biradicals.

Our previous work on the reaction of aliphatic dihalides ⁴ with excess sodium led us to the conclusion that a biradical was formed and that the radical underwent either cyclisation to a saturated or isomerisation to an unsaturated molecule.

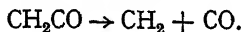
For example :



In the present work the reaction, $RCl_2 + 2Na \rightarrow 2NaCl + R<$, has been used to prepare and study the reaction of methylene and biradicals having up to six carbon atoms.

Methylene and Ethylidene.

Methylene.—There is much direct evidence for the existence of free methylene. Norrish, Crone and Saltmarsh,⁵ and later, Ross and Kistiakowsky,⁶ postulated its formation in the photolysis of ketene :



The direct proof of its formation was supplied by examination of the interaction of the products of the decomposition of diazomethane ⁷ and methane ⁸ with tellurium and iodine mirrors respectively. More recently, Pearson, Purcell and Saigh,⁹ using a similar technique, have shown very conclusively that methylene is produced in the photol and thermal decomposition of both diazomethane and ketene. The latter authors conclude, in agreement with Norrish,⁵ that methylene has the nature of a molecule rather than a free radical and that its structure corresponds to the divalent state of atomic carbon. This conclusion was confirmed by Bawn and Dunning,⁴ who, in order to explain the chemiluminescence of the reaction of sodium and methylene halides, postulated the direct formation of methylene in the ¹A state.

² Polymerisation Discussion, *Trans. Faraday Soc.*, 1935, **32**, 54, etc.; Hurd, *Ind. Eng. Chem.*, 1934, **26**, 50.

³ Bamford and Norrish, *J. Chem. Soc.*, 1938, 1521; Saltmarsh and Norrish, *ibid.*, 1935, 455.

⁴ (a) Bawn and Hunter, *Trans. Faraday Soc.*, 1938, **34**, 608; (b) Bawn and Dunning, *ibid.*, 1939, **35**, 185.

⁵ Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1933, 1533.

⁶ Ross and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1112.

⁷ Rice and Glasebrook *ibid.*, 2381.

⁸ Belchetz, *Trans. Faraday Soc.*, 1934, **30**, 170; Belchetz and Rideal, *J. Amer. Chem. Soc.*, 1935, **56**, 1168; *ibid.*, 2466.

⁹ Pearson, Purcell and Saigh, *J. Chem. Soc.*, 1938, 409.

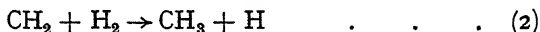
In spite of the fact that the normal state of methylene is one in which there is no unpaired electron, it is known to be very reactive. Thus, it combines readily with itself to give ethylene⁴ and reacts rapidly with diazomethane.⁹ Its rapid disappearance in methane⁸ must be ascribed to a reaction with that gas. It also combines with carbon monoxide to give ketene,¹⁰ and with molecular oxygen¹¹ yielding the intermediate CH_2O_2 . In the present work we find that methylene also reacts rapidly with hydrogen at 300° C. with the formation of methane.

Reaction of Methylene with Hydrogen.—Methylene was prepared by the reaction of methylene bromide with sodium vapour, and in nitrogen the product of the reaction was ethylene, formed by the dimerisation of the methylene. When the reaction was carried out in hydrogen, however, the latter gas was rapidly used up, as could be observed by the decrease of pressure in the reaction vessel. Analysis of the products showed them to be mainly methane together with a small amount of ethylene. The methane was obviously formed by the direct association of methane and hydrogen,



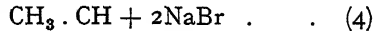
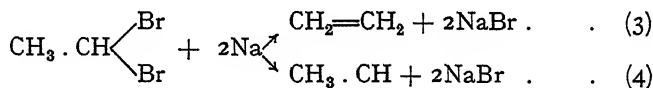
The possibility that this reaction occurs at the surface of the vessel cannot be excluded at present.

This high reactivity with hydrogen is predictable from thermochemical evidence. Voge¹² has calculated theoretically the energy of formation of CH_2 and CH_3 as 184 and 278 cal. respectively. The value for CH_2 cannot be much in error since it would be twice the energy of the C—H molecule (~ 91 cal.) which is known from spectroscopic data. Taking the energy of formation of methane as 391 cal., reaction (1) would be 80 cal.* exothermic, whereas from Voge's data for CH_3 the alternative reaction,



is 19 cal.* endothermic. The activation energy of (2) will be at least equal to the endothermicity and this is probably much greater than the activation energy of the highly exothermic reaction (1).

Ethylidene.—Although the ethylidene radical has often been postulated in hydrocarbon reaction mechanisms, there is as yet no experimental evidence pointing to its existence.¹³ In our experiments the product of the reaction of ethylidene chloride and bromide was ethylene, formed either directly or by the isomerisation of the ethylidene radical:



No butylene (which would be formed by dimerisation) was ever found in the products as expected by analogy with methylene if the $\text{CH}_3\text{CH} \cdot$ radical were formed. Furthermore, in order to account for the chemiluminescence of the reaction,^{4(b)} it was necessary to assume that reaction

* After correcting Voge's data for zero-point energy.

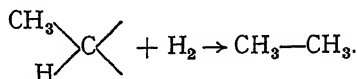
¹⁰ Staudinger and Kupfer, *Ber.*, 1912, 45, 501; Rice and Glasebrook, *J. Amer. Chem. Soc.*, 1934, 56, 741.

¹¹ Gregory and Style, *Trans. Faraday Soc.*, 1936, 32, 724.

¹² Voge, *J. Chem. Physics*, 1936, 4, 581.

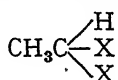
¹³ Rice and Glasebrook, *J. Amer. Chem. Soc.*, 1934, 56, 741.

(3) occurred to a small extent. The electronic state of the ethylidene molecule is by analogy with methylene 1A , and as with the latter molecule, it may be assumed that if $\text{CH}_3\text{CH}<$ is formed at all it would react with hydrogen forming ethane:



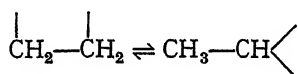
The results of the study of reactions (3-4) in hydrogen showed ethylene as the only product, and that no ethane was formed. It is concluded, therefore, that the true course of the reaction is represented by (3) and that neither the free ethylidene molecule or radical is ever formed.

Since any attempt to prepare ethylidene from a saturated



molecule involves the breaking of one or both of the C—X bonds, it is apparent that this process will require a far less activation energy if accompanied by the simultaneous formation of the double bond. It is unlikely, therefore, that the ethylidene will be formed in thermal reactions except at very high temperatures.

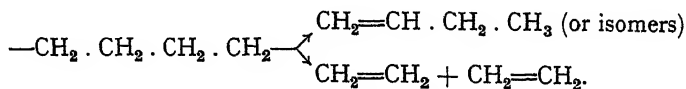
It may be formed in processes involving the opening of a double bond when an equilibrium of the type,



is possible.

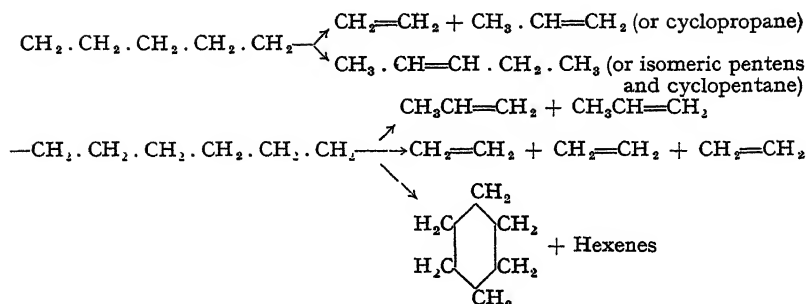
Tetramethylene and Higher Radicals.

In contrast to mono- and dimethylene and ethylidene, the experimental facts indicate that trimethylene and its higher homologues are formed in the free radical state. Thus, the reaction of 1:4 dibromo-*n*-butane gives ethylene (41 per cent.) and butylene (59 per cent.) as products. The most satisfactory explanation of this reaction is to assume that the tetramethylene radical is produced, and can decompose to give ethylene or to rearrange to give butylene.



On the other hand, in the case of 1:2 dibromo-*n*-butane, in which the unsaturated molecule can be formed in the same process as the removal of the second bromine by simple closure of the double bond, there seems to be no reason to postulate the intermediate formation of a biradical.

As with 1:4 dibromo-*n*-butane, 1:5 dibromo-*n*-pentane, and 1:6 dibromo-*n*-hexane give rise to two sets of products, the formation of which can be interpreted as alternative decompositions of the radical according to the following scheme:

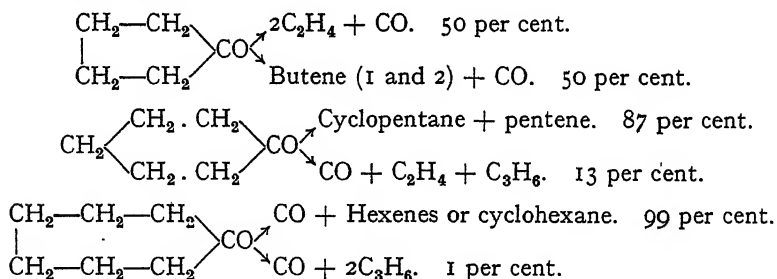


The comparison of these results (see also Table I) with those of Norrish

TABLE I.

Dihalide.	Carrier Gas.	Products per cent.						
		CH ₄ .	C ₂ H ₄ .	C ₂ H ₆ .	C ₃ H ₈ .	C ₄ H ₈ .	C ₅ H ₁₀ .	C ₆ H ₁₂ .
CH ₂ Cl ₂ , CH ₂ Br ₂ , CH ₂ I ₂	N ₂	—	100	—	—	—	—	—
	H ₂	92	8	—	—	—	—	—
CH ₃ CHCl ₂ , CH ₃ CHBr ₂	N ₂	—	100	—	—	—	—	—
	H ₂	—	100	—	—	—	—	—
BrCH ₂ (CH ₂) ₂ CH ₂ Br	N ₂	—	41	—	—	59	—	—
BrCH ₂ —CHBr—CH ₂ —CH ₃	N ₂	—	—	—	—	100	—	—
BrCH ₂ (CH ₂) ₃ CH ₂ Br	N ₂	—	10	—	10	—	80	—
BrCH ₂ (CH ₂) ₄ CH ₂ Br	N ₂	—	small	—	small	—	—	>95

and Bamford¹⁴ on the photol decomposition of cyclic ketones is very striking. These authors found that cyclic ketones decomposed in the following manner :



and assumed that the hydrocarbons were the decomposition products of the corresponding biradicals formed by the elimination of carbon monoxide from the ketone. The almost complete identity of their products with those obtained in this work provides additional support for this assumption.

Experimental Method and Results.

The apparatus used was a modified form of that already described,^{4(a)} the important change in construction being the introduction of both the sodium and the halide into the reaction vessel in a stream of nitrogen.

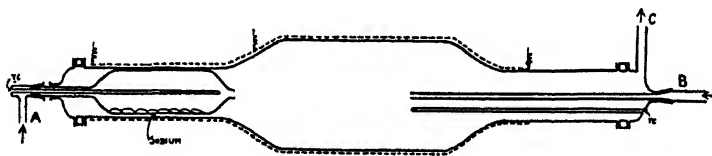
¹⁴ Steacie and Phillips, *J. Chem. Physics*, 1936, 6, 179.

Conditions were so arranged that there was negligible back diffusion of sodium into the nozzle from which the halide entered. The pressures of the reactants were adjusted such that the sodium was in large excess.

The temperatures of the sodium container and of the reaction vessel were measured by an inserted thermocouple, and were maintained at 290° and 300° C. respectively in all experiments. The pressure of the carrier gas employed was 5-7 mm. Hg.

The design of the reaction system is shown in the Fig. The dimensions of the centre portion in which the reaction occurred were 7 cm. diameter and 15 cm. length. Two forms of flow system were employed, (a) direct flow and (b) circulating flow. In both methods the total flow was divided into two streams, one entering at A and passing over the sodium and the other carrying the halide into B. The relative amounts of gas flowing into A and B were fixed by the use of suitable capillary tubes. Before entering B the stream passed through a saturator containing the halide, the latter being maintained at constant temperature (which varied from -10° to -78° C. according to the halide used) throughout the run. The flow was measured by a flowmeter containing butyl phthalate. The products were collected in two traps cooled at -186° C. and about -217° C. (pumped out liquid oxygen) respectively, and were distilled *in vacuo* into a third and smaller trap from which they could be removed by a Toepler pump.

The products were separated into fractions according to their volatility, by cooling the latter trap with suitable low temperature baths and pumping off the volatile substances. In separating C₄ and higher hydrocarbons, it was found necessary to mix with nitrogen gas to avoid condensation in the



Toepler pump. The cooling baths employed were liquid oxygen, melting pentane (-150° to -160° C.), solid acetone (about -100° C.), solid carbon dioxide and acetone (-78° C.). In later experiments the low temperature apparatus described by Steacie and Phillips¹⁴ was found highly satisfactory for temperatures in the range -100° to -160° C.

The gaseous products, H₂, CH₄, C₂H₆, C₂H₄, and higher unsaturated hydrocarbons were analysed by fractional combustion over copper oxide. Unsaturation was determined by absorption with bromine and carbon dioxide by potash absorption. The experimental details of the analytical procedure were as described by Broom¹⁵ and Travers and co-workers.¹⁶

Results.—The results of many experiments with methylene chloride, bromide and iodide using N₂ as the carrier gas showed ethylene as the only analysable product. In separating the ethylene, the nitrogen was pumped off with the cooled trap at -217° C. and the ethylene removed at -78° C. The gas combusted as a C₂ hydrocarbon and was completely absorbed by bromine in aqueous KBr. There was also some evidence of the formation of some non-volatile product,—probably a polymer of CH₂ or ethylene.

The procedure was slightly different when H₂ was used as carrier gas. At the end of the run, most of the methane which had collected in the trap at -217° C. together with any hydrogen in the trap was pumped off at -186° C. Ethylene was then obtained by warming to -78° C. The composition of the products was 92 per cent. CH₄ and 8 per cent. C₂H₄. The general practice of separating the products of the reaction of C₄, C₅ and C₆ dihalides was to remove the nitrogen at -186° C., then C₂ and C₃

¹⁵ Broom, *J. Soc. Chem. Ind.*, T, 1928, 47, 276.

¹⁶ Travers and Hockin, *Proc. Roy. Soc.*, 1932, 136, 1.

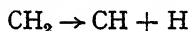
hydrocarbons at -140° to -150° C. and C_4 at -78° C. With the reaction of 1 : 5 dibromo-*n*-pentane, the lower hydrocarbons were removed at -96° to -100° C. and C_5 at -78° C. Since only small amounts of gas were available, the C_2 and C_3 hydrocarbons were not separated and were therefore combusted together. Attempts to determine the melting-points of the hydrocarbon products from 1 : 5 dibromo-*n*-pentane were not very successful since the products invariably set as a glass on cooling. The part volatile at -96° C. combusted as a C_5 hydrocarbon and was entirely absorbed by bromine in aqueous KBr. The product was certainly not pure cyclopentane (M.-Pt. -93° C.) since it was liquid at -120° C. It probably is a mixture of this substance and amylene (M.-Pt. approx. -130° to -140° C.).

The reaction of 1 : 6 dibromo-*n*-hexane gave little gas volatile at -80° C. The main product melted at 0° to 1° C. and combusted as a C_6 hydrocarbon. It may therefore be identified as cyclohexane (M.-Pt. 6.5° C.) with possibly some hexene.

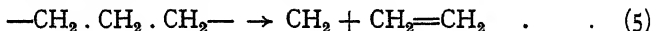
The results are summarised in Table I.

Discussion.

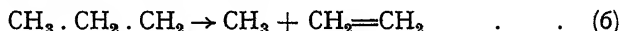
The methylene molecule should be extremely stable thermally since the primary dissociation process :



is about 90 cal. endothermic. The trimethylene radical, on the other hand, decomposes much more easily since the $C-C$ bond, which is 15-20 cal. weaker than the $C-H$ bond, can break with the simultaneous formation of an unsaturated molecule :

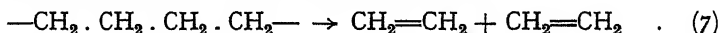


The energy liberated in the closure of the double bond causes a considerable lowering of the activation energy below that required for the simple rupture of a $C-C$ bond. By comparison with the analogous decomposition of the propyl radical,¹⁷ viz. :

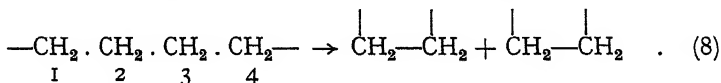


the theory of which has been examined previously, the energy of activation of (5) is about 30 cal.

In the case of tetramethylene there is an additional source of energy if the radical dissociates to two ethylene molecules :



The activation energy of this change can be estimated by the methods previously worked out for monoradicals.¹⁷ This involves the calculation of two energy surfaces corresponding to the two different states of the system. The first surface corresponds to the reaction :

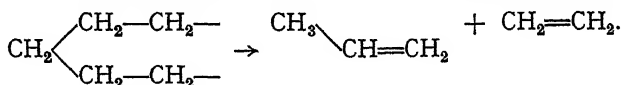


and will represent the energy as a function of the C_2-C_3 bond separation for the different separations $r_{C(1)-C(2)}$. Since the bonds C_1-C_2 and C_3-C_4 are equivalent, the surface can be represented in terms of these two co-ordinates.

¹⁷ Bawn, *Trans. Faraday Soc.*, 1938, 34, 598. We wish to thank M. Banan who carried out this calculation.

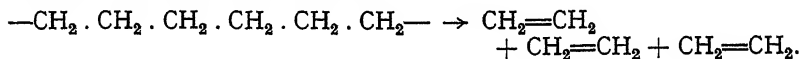
The surface corresponding to reaction (8) does not give the true final state of the system. This will lie in a valley on the energy surface corresponding to the formation of ethylene in its normal state. This second surface will be of a different form from the above since the interaction between two normal ethylene molecules gives rise to strong repulsive forces. The latter surface can be constructed in terms of the same co-ordinates as surface I. The true energy surface can then be obtained by combining these two surfaces in such a way that the initial and final valleys are separated by an energy height equal to the heat of reaction (7). The formulæ employed and further details of the method of calculation can be found in the paper referred to above.¹⁷ Using values of D_{C-C} , 73.4 cal. and $D_{C=C}$, 138 cal. and a radius of CH_2 , 1.40 Å., the activation energy is found to be 15 cal.

The pentamethylene radical can decompose in a similar manner to tetramethylene, giving propylene or cyclopropane and ethylene.



This process may have a slightly greater activation energy than (7) on account of the shift of the hydrogen atom.

The hexamethylene radical gives rise to a new possibility in that the molecule may split up with the breaking of two C—C bonds, and the formation of three double bonds.



The activation energy of this reaction will be intermediate between that of the tri- and tetramethylene. In this case we have also to consider the possibility that processes involving the breaking of more than one or two non-adjacent bonds may be very improbable. We have also the alternative decomposition reaction :



Again, on account of the isomerisation, the activation energy will be higher than that of tetramethylene.

It may be concluded from this qualitative theory of the various decomposition processes that the minimum in the stability of the $(CH_2)_n$ chain up to $n = 6$, occurs with $(CH_2)_4$, as indicated by our experimental results.

Summary.

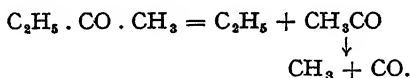
The reaction of sodium with aliphatic dihalides has been used to prepare methylene and biradicals containing up to six carbon atoms. Methylene reacts with H_2 at 300° C. to give methane. No evidence for the formation of ethylidene was obtained. The decomposition products of tetra, penta, and hexamethylene radicals have been determined and the stability of these radicals discussed.

The authors express their thanks to Imperial Chemical Industries Ltd. and to the Colston Research Society for grants for the purchase of apparatus, and to the Department of Scientific and Industrial Research for a maintenance grant to one of them (J.M.).

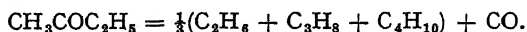
*Department of Physical Chemistry,
The University, Bristol.*

GENERAL DISCUSSION.*

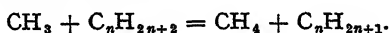
Prof. R. G. W. Norrish (*Cambridge*) said: There is evidence that when free hydrocarbon radicals are liberated in a medium consisting of hydrocarbon molecules, ready exchange of hydrogen atoms occurs between the radicals and the molecules at temperatures exceeding 80° C. This is shown by a comparison of the photochemical decomposition of ketones in the vapour phase with the corresponding decomposition in paraffinoid solution. It is well known, for example, that methyl ethyl ketone is decomposed by light of wave-length 2800 Å at 80° C. to give free radicals of methyl and ethyl¹



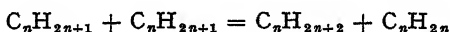
In the gas phase the methyl and ethyl radicals combine among themselves to give a mixture of the three hydrocarbons ethane, propane, and butane, so that the net result of the photochemical change is given approximately by the equation



In liquid paraffin, or iso-octane solution, however, the products are different and at 80°-100° C. the hydrocarbons consist almost completely of methane and ethane² in equimolecular proportion. This arises from the fact that at this temperature the hydrocarbon radicals readily hydrogenate themselves at the expense of the paraffinoid solvent to the practical exclusion of recombination, *e.g.*,



The value of the energy of activation for this process occurring between propyl radicals and iso-octane molecules was found by Bamford and Norrish³ to be of the order 12.3 k.cals., and while it takes place rapidly at 100° C., it is extremely slow at room temperature. Further, the heavy free hydrocarbon radicals react ultimately by disproportionation—



for unsaturation equivalent to the original photolysis can be titrated in the solvent after it has been freed from the unchanged ketone.

From this we may assume that at temperatures over 100° C., there is a ready exchange of hydrogen between molecules and of heavy free hydrocarbon radicals until the unsaturation is finally stabilised by the disproportionation reaction when two radicals meet. With light hydrocarbon radicals in the gas phase, however, the tendency is almost exclusively towards recombination rather than disproportionation, as is shown by the production of saturated hydrocarbons in the photolysis of acetone, methyl ethyl, diethyl, methyl propyl, and dipropyl ketones in the gas phase.

This difference between the interactions of light and heavy hydrocarbon radicals may arise from causes of orientation; for with two large or complicated radicals it is unlikely that a collision will bring their reactive ends into sufficient proximity for recombination. Thus exchange of hydrogen, and reaction by disproportionation will be favoured. With two simple hydrocarbon radicals, however, collision will generally bring their active ends into sufficient proximity for reaction by recombination to ensue.

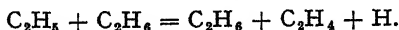
* On the three preceding papers.

¹ Norrish and Appleyard, *J.C.S.*, 1934, 874.

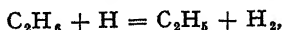
² Bamford and Norrish, *ibid.*, 1938, 1531.

³ *Ibid.*, 1938, 1544.

It may be noted that at still higher temperature there is the possibility that another reaction between free hydrocarbon radicals and molecules may intervene :



Such a reaction, coupled with the reaction



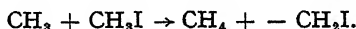
would make possible the chain propagation by hydrogen atoms postulated by Hinshelwood and his collaborators in the decomposition of ethane and other paraffins to olefine and hydrogen.⁴

Dr. C. E. H. Bawn (*Bristol*) said : I would like to mention an additional result we have obtained since our paper was written. When methylene is liberated in methane (used as carrier gas) it has been found that the reaction



does not occur to a measurable extent at 300° C. This conclusion follows from the analysis of the reaction products, which were found to be entirely ethylene, with little or no ethane.

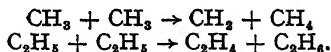
Some other investigations of the reactions of methyl radicals carried out with Dr. W. J. Dunning show that CH_3 prepared by the reaction of atomic sodium with excess methyl bromide reacts with the halide according to



The temperature coefficient of the rate of the reaction gave an activation energy of 12 Cal. This value is a very good approximation to the activation energy of the reaction of methyl with hydrocarbons, *e.g.*



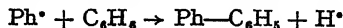
At temperatures up to 350° C., CH_3 and C_2H_5 radicals have been found to react with themselves only by an associated mechanism, giving ethane and butane respectively. Detailed analyses of the reaction products have shown no evidence of the disproportionation reactions,



Dr. W. A. Waters (*Durham*) said : The general reaction of a free alkyl radical with an aliphatic hydrocarbon, either in the gaseous phase or in solution, is a hydrogenation, *viz.*,



Free aryl radicals, which can be produced in many solvents, react similarly with aliphatic molecules, *e.g.*, $\text{Ph}\cdot + \text{H}-\text{R} \rightarrow \text{Ph}-\text{H} + \cdot\text{R}$, but in aromatic solvents the reaction is quite different, for the aryl radical reacts with a carbon atom and not with a hydrogen atom, *e.g.*,



Free radical reactions of this latter type may be used for the synthesis of polyaryls.⁵

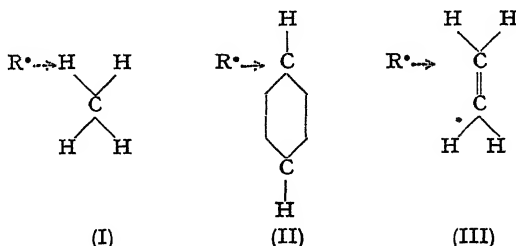
What theoretical explanation can be given for this marked difference in the behaviour of aliphatic and aromatic molecules ?

One can see that collisions of free radicals with paraffins are inevitably collisions with hydrogen atoms which completely surround the carbon

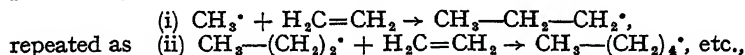
⁴ See Staveley and Hinshelwood. Paper 6 of this discussion.

⁵ Grieve and Hey, *J. Chem. Soc.*, 1938, 108; 1934, 1797. Waters, *ibid.*, 1939, 866.

skeleton (I), whilst some collisions with aromatic molecules may be collisions with nuclear carbon atoms (II).



However, from a stereochemical picture of this simple type, one might infer that a free radical should add on to, or substitute hydrogen in, an olefine (III), but simple reactions of these latter types do not seem to occur (unless one places the Diels-Alder diene addition reaction into this category). It is quite true that the methyl radical can bring about the chain polymerisation of C_2H_4 , and one can represent this as a chain addition process, *e.g.*,

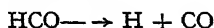


but simple addition reactions of hydrocarbon radicals, analogous to additions of halogen atoms, are not yet known.

Dr. D. W. G. Style (*London*), said: Some experiments carried out with Summers show that the photo-decomposition of formaldehyde is accelerated by the addition of hydrogen and nitrogen at temperatures above 100° . The temperature coefficient of the acceleration corresponds to an activation energy of 12 Cals. We are inclined to ascribe the acceleration to the reaction $\text{M} + \text{HCO} = \text{H} + \text{CO} + \text{M}$.

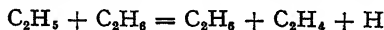
This activation differs widely from that of Gorin, who assumes the decomposition to be monomolecular and we would like to ask Bawn if he has calculated the activation energy of the decomposition of formyl.

Dr. C. E. H. Bawn (*Bristol*), in reply, said: There is much uncertainty attached to calculations of the activation energy of decomposition of the formyl radical on account of our lack of knowledge of the real values of the C—H bond strength in HCO — and of the energy of the transition $>\text{C}=\text{O} \rightarrow \text{C}\equiv\text{O}$. Assuming $D_{\text{C-H}} = 80$ Cal. and that the above transition is 80 Cal. exothermic, we estimate by the methods used previously⁶ that the activation energy of the reaction



is 19.5 Cal. Theoretically this value could be brought into agreement with the experimental value of Style if $D_{\text{C-H}}$ were less than 80 Cal., which is improbable, or if the transition $\text{C}=\text{O} \rightarrow \text{C}\equiv\text{O}$ were 90 Cal. or more exothermic.

Dr. L. K  chler (*G  ttinger*) said: Norrish assumes that the reaction



may intervene as one step in the chain decomposition of ethane. This is very improbable, since it does not seem possible to give any special mechanism of the ethane decomposition involving that reaction, which yields the first order and does not conflict seriously with other experimental results.

⁶ Bawn, *Trans. Faraday Soc.*, 1938, **34**, 598.

THE INFLUENCE OF TEMPERATURE ON THE STABILITY OF A MINERAL OIL.

BY F. P. BOWDEN, L. LEBEN, AND D. TABOR.

Received 21st March, 1939.

The physical and chemical changes that occur when a mineral oil is heated are very complex and there is a large literature dealing with the subject. These changes are of special interest in the case of a lubricating oil. In a running engine the oil is heated over a range of temperatures and the changes may influence its lubricating properties.

In general a saturated hydrocarbon will not be strongly adsorbed at a metal surface and will be a poor boundary lubricant. If unsaturated compounds or polar bodies are formed the lubricating properties may be improved. There is some indication that the lubricating properties of an oil are improved by heating. King¹ found that the friction of an oil was lowered and its seizing temperature raised when the oil was heated to a high temperature in the presence of oxygen. The friction was measured in an actual bearing. Its very low value ($\mu = 0.00045$), however, suggests that the conditions were mainly those of fluid lubrication. Stager,² Gilson,³ Dover and Appleby⁴ and others have also suggested that the oil is improved by heating or by oxidation. The changes occurring are very complex and may be greatly influenced by the atmosphere, by the surface, or by the presence of traces of foreign substance (see Gilson,³ Pye,⁵ Moerbeek,⁶ Hanson and Egerton,⁷ Moutte, Dixmier, and Lion⁸).

A recent analysis⁹ of the kinetic friction between steel surfaces lubricated with a boundary film of mineral oil has shown that the frictional force does not remain constant during sliding. The sliding is not a continuous process; the motion proceeds in jerks and it is clear that an intermittent clutching and breaking away of the metal is occurring through the oil film. The addition of certain compounds to the oil may alter this behaviour. The addition of a few per cent. of a long chain fatty acid for example may stop this "stick-slip" and allow continuous sliding to occur. At the same time the wear of the surfaces is reduced. The exact nature of the sliding, *e.g.* whether it is continuous or intermittent is of greater significance than the actual value of the coefficient of friction and this analytical method provides a sensitive test for the lubricating properties of a substance. This method was used to follow the changes which occur when a mineral oil is heated, to investigate whether lubricating substances are in fact formed, and if so, to determine

¹ King, *Proc. Roy. Soc., A*, 1933, 139, 447.

² Stager, *Int. Com. Test. Mat.*, Amsterdam, 1927, 2, 456.

³ Gilson, *Ind. Eng. Chem.*, 1926, 18, 467.

⁴ Dover and Appleby, *ibid.*, 63.

⁵ Pye, *The Internal Combustion Engine*, Oxford Univ. Press, 1934, Vol. 2.

⁶ Moerbeek, General Discussion on Lubrication and Lubricants, *Institution of Mechanical Engineers*, Group IV, Properties and Testing, 1937, p. 146.

⁷ Hanson and Egerton, *ibid.*, p. 122.

⁸ Moutte, Dixmier and Lion, *ibid.*, p. 151.

⁹ Bowden and Leben, *Proc. Roy. Soc., A*, 1939, 169, 371.

TIME: 1 DIV. = 0.5 SEC.

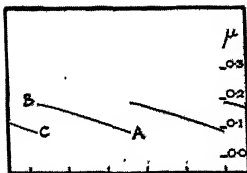


FIG. 1. MINERAL OIL
15°C.

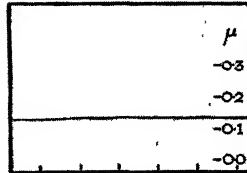


FIG. 2. MINERAL OIL
+ 1% CAPRYLIC ACID

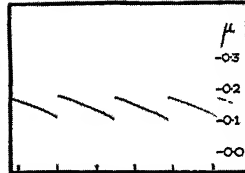


FIG. 3. MINERAL OIL
100°C.

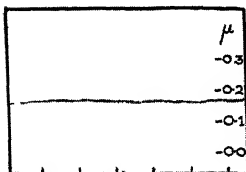


FIG. 4. MINERAL OIL
200°C.

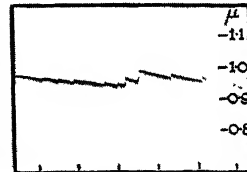


FIG. 5. MINERAL OIL
300°C.

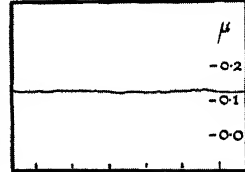


FIG. 6. MIN. OIL HEATED
200°C. & COOLED

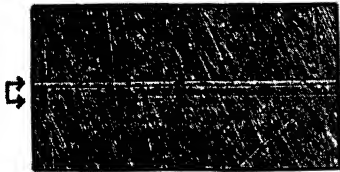


FIG. 7. MINERAL OIL 15°C.

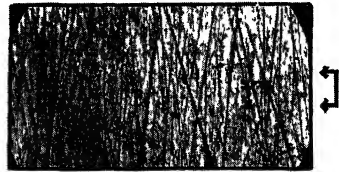


FIG. 8. MINERAL OIL +
1% CAPRYLIC ACID

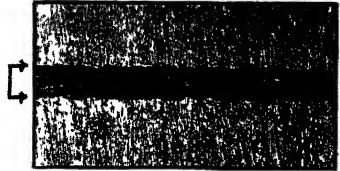


FIG. 9. MINERAL OIL 300°C.

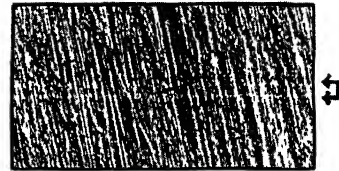


FIG. 10. MINERAL OIL HEATED
200°C. & COOLED

Figs. 7-10. Magnification of Track = 50.

[To face page 901.

with greater precision the temperature and conditions under which this takes place.

The experiments were of two types. In the first type the oil was applied as a thin film to the steel surfaces which were then raised to the required temperature. In the second type the oil was heated in bulk for a definite time in the presence and in the absence of air. The oil was then cooled down and applied to the steel surfaces at room temperature.

Experimental.

The apparatus has been described elsewhere.⁹ The lower surface was a flat steel plate which was driven at a uniform rate by a water piston. The temperature of this surface could be raised by means of an electric heating element incorporated in the apparatus. The upper surface which rested on the plate was a small curved steel slider which was attached to a high frequency device for measuring the frictional force and for recording photographically any fluctuations in it if they occurred. The steel surfaces were prepared by fine grinding and lapping on lead laps with 320 carborundum and were carefully cleaned. The speed of the lower plate in these experiments was approximately 0.003 cm./sec. and the applied load was varied from 400 to 4000 gms. The behaviour was essentially the same at all the speeds and loads used. The mineral oil used was a purified "white oil." It was principally naphthenic and contained about 3 per cent. of aromatic compounds.

Results.

The Effect of Adding a Fatty Acid.

A typical photographic trace showing the frictional behaviour of the pure white oil on the steel surfaces at room temperatures is shown in Fig. 1. The passage of time is from right to left. The tangential force between the surfaces is recorded by the trace. This tangential force divided by the normal load gives the coefficient of friction and the value of this is marked on the ordinates. The trace therefore represents the fluctuations of the friction with time. These fluctuations all consist of a period AB during which the tangential force is increasing steadily followed by a very rapid fall BC. A measurement of the slope of the line AB shows that the top surface is moving forward with the same velocity as the bottom one, *i.e.*, there is no relative motion of the surfaces, they are sticking together. Suddenly a very rapid slip of the upper surface occurs. When the tangential force has fallen to C the surfaces again stick and the process is repeated indefinitely. It will be seen that the coefficient of friction varies between $\mu = 0.1$ and 0.2 and the average value is about $\mu = 0.15$. The track formed on the steel plate when the slider has passed over it once is shown in Fig. 7.

The effect of adding 1 per cent. of caprylic acid to the oil is shown in Fig. 2. It will be seen that the large "stick-slips" have disappeared and within the limit of the observation the sliding is continuous. The value of the friction is $\mu = 0.13$. The track formed under these conditions is shown in Fig. 8. It lies between the arrows and is barely visible on the photograph. It is clear that the wear is considerably reduced.

Effect of Heating Oil on Surface.

A thin film of oil was placed on the surface at room temperature. The frictional behaviour showed stick slips similar to Fig. 1. After standing for 12 hours the frictional behaviour was still the same. The surface was then recleaned and warmed to 100° C. Oil was applied to the surface and the friction determined after regular intervals of time had elapsed. It was found that motion still proceeded by stick slips and no appreciable

change was observed during continued heating over a period greater than 2 hours. A typical trace is shown in Fig. 3. The experiment was then repeated, this time at a higher temperature of 150°C . On first applying the oil stick-slips, essentially similar to those obtained at lower temperatures were observed. After 30 minutes heating, however, a change in the nature of the sliding was found to have occurred. The friction was similar to that shown in Fig. 4, and it will be seen that continuous sliding was taking place between the surfaces. At the same time the wear between the surfaces was considerably reduced. The wear was now similar to that shown in Fig. 10. No further change in the friction and wear occurred on further heating of the oil for periods longer than 2 hours. At a higher temperature (200°C .) a similar change-over from stick slips to sliding occurred (see Fig. 4) but in this case the change was more rapid (15 minutes). At 300°C . the change was much more rapid still and in 2 minutes continuous sliding was observed. When the heating was continued for 20 minutes, however, a further change took place. The oil formed a thick gum, the friction rose to a high value and stick-slips again occurred (Fig. 5). At the same time the track showed greatly increased wear (Fig. 9).

A second experiment was performed in which the temperature of the steel plate was raised to 200°C . and the oil heated until continuous sliding set in. The surface was then cooled to room temperature and it was found (Fig. 6) that continuous sliding still occurred. The oil under these conditions also continued to afford better protection to the surface (see Fig. 10). This shows that the heating has produced some irreversible change either in the oil or in the surface. The oil was then washed gently off the surface with acetone and fresh unheated oil was added. Stick-slip now occurred. This suggests that the irreversible change had taken place in the oil itself.

Effect of Heating the Oil in Bulk.

10 c.c. samples of the mineral oil were placed in glass tubes and heated to the required temperatures in oil baths. Specimens were withdrawn at different intervals of time and the frictional behaviour studied. Three series of experiments were carried out. In the first series the oil was saturated with air by passing a slow stream of dry air through it. In the second air was excluded by evacuating and sealing the tubes. In the third a stream of ozone was bubbled through the oil at 0°C . The results are collected in Table I.

TABLE I.

	Temp.	Time.	Frictional Behaviour.	Colour.]
	$^{\circ}\text{C}$.	Mins.		
Series 1. Saturated with air	15	> 120	Stick slip	Colourless
	150	60	Stick slip	Faint yellow
		90	Stick slip, occasional sliding	
		240	Sliding	
	200	60	Sliding, occasional stick slip	Yellow
		240	Sliding	Yellow
	300	< 60	Sliding	Dark brown
		300	Stick slip	
Series 2. Air excluded	200	60	Stick slip	Colourless
	300	540	Stick slip	Almost colourless
Series 3. Ozone passed	0	15	Stick slip	Colourless
	0	30	Stick slip, occasional sliding	Almost colourless
	0	60	Sliding	Almost colourless

Discussion.

These experiments show that when a mineral oil is heated compounds are formed which improve its lubricating properties so that the frictional behaviour changes over from stick slip to continuous sliding. The addition of 1 per cent. of fatty acid will cause a similar change to continuous sliding.

At low temperatures the rate of formation of these compounds in the oil is very slow. At room temperature no change was observed in twelve hours although the oil was spread as a thin film on the steel surface. At 100° C. no change in the oil film was observed after two hours. At 150° C., however, the change from "stick-slip" to continuous sliding occurred in thirty minutes. At 200° C. it occurred in fifteen minutes and at 300° C. it took place in two minutes. It is clear that the rate of formation of these compounds is greatly accelerated by a rise in temperature. At temperatures up to 200° C. the oil film maintains its lubricating properties after prolonged heating. At 300° C., however, further rapid changes take place. Most of the oil is driven off and stick-slip occurs with the residue on the surface.

When the oil was heated in bulk in the presence of air very similar changes occurred but the process was very much slower. At 150° C. for example two to four hours were necessary before the polar compounds were formed in sufficient quantity to give continuous sliding. Again the rate of formation was accelerated by a rise in temperature and at 200° C. one hour was sufficient. At 300° C. the formation was more rapid still but on continued heating these compounds were decomposed and other deleterious ones formed so that the lubricating properties were destroyed and stick slip again set in. The time for this change in the bulk oil was five hours as compared with the few minutes required for the oil film. It is clear that the changes in the oil are due to oxidation. If oxygen is excluded no lubricating substances are formed and no change can be detected even on heating for nine hours at 300° C. In the presence of ozone the changes occur rapidly at 0° C. The rapid rate of formation of these compounds on the steel compared with the relatively slow rate of formation in the bulk of the oil suggests that the formation may be catalysed by the steel surface.

The substances responsible for the frictional changes are not necessarily coloured. The oil which had been ozonised was almost colourless yet it gave continuous sliding. The oils which gave sliding showed an increase in absorption in the ultra-violet and they had a smell which resembled that of the shorter fatty acids. No attempt at chemical analysis of the oils was made. The influence of water vapour was not studied. So far only one oil has been investigated in detail but other oils showed similar behaviour.

The fact that these compounds are so readily formed on metal surfaces means that they are probably produced *in situ* in certain parts of a running engine, e.g. on the piston rings and cylinder walls. A fresh oil may be a worse lubricant than an old one. The results suggest that, if the temperature is round about 200° C. the compounds are produced quite rapidly and may decrease the friction. It does not follow of course that the resultant effect of these compounds will be beneficial. Their subsequent harmful properties of polymerisation, gumming, corrosion, etc., may outweigh the frictional reduction. At temperatures near 300° C. the compounds produced may cause increased friction and wear.

Experiments ¹⁰, ¹¹ have shown that, even if the metals are cold the local temperatures at the points of sliding contact may be very high so that even on cold metals a local formation of the compounds may take place.

These observations also have an important bearing on the testing of lubricating substances. When, for example, a substance is added to an oil and tested at different temperatures the frictional changes observed may be due more to the compounds formed in the oil itself than to the influence of the added dope.

Figs. 2 and 8 show that the presence of a trace of fatty acid in a mixture may reduce the friction and wear between steel surfaces. This is true for cool and for relatively slow moving surfaces. Other experiments have shown that on *hot* metal surfaces the friction and wear with an oil containing added fatty acid may be *greater* than that observed with an undoped oil.

We wish to express our thanks to the Royal Society and to the Chemical Society for grants for apparatus.

Summary.

When a mineral oil is heated in the presence of air, compounds are formed in it which have a profound effect on its lubricating properties. These compounds change the frictional behaviour from "stick-slip" to continuous sliding and reduce the wear.

The rate of formation of these compounds is much more rapid when the oil is present as a thin film on a steel surface than it is in bulk. The rate of formation is very dependent upon temperature. At room temperature or at 100° C. the rate is slow even in a thin film, but it increases rapidly as the temperature rises and at 200° C. it may be fast. At temperatures near 300° C. other compounds are formed which decrease the lubricating properties of the oil.

These observations have an important bearing on the behaviour of a lubricating oil in a running engine and on the testing of lubricants.

*Laboratory of Physical Chemistry,
Cambridge.*

GENERAL DISCUSSION.

Prof. H. I. Waterman (*Delft*) said: Are the characteristics of the mineral oil used by Bowden known? In the paper the mineral oil was stated to be a purified "white oil" of the medicinal paraffin type. It seems that this identification is not sufficient.

Such a white oil can vary in percentage of rings or in paraffinic side chains. Why are the specific gravity, the refractive index, the aniline point, and other constants of the raw material not determined in order to identify the product?

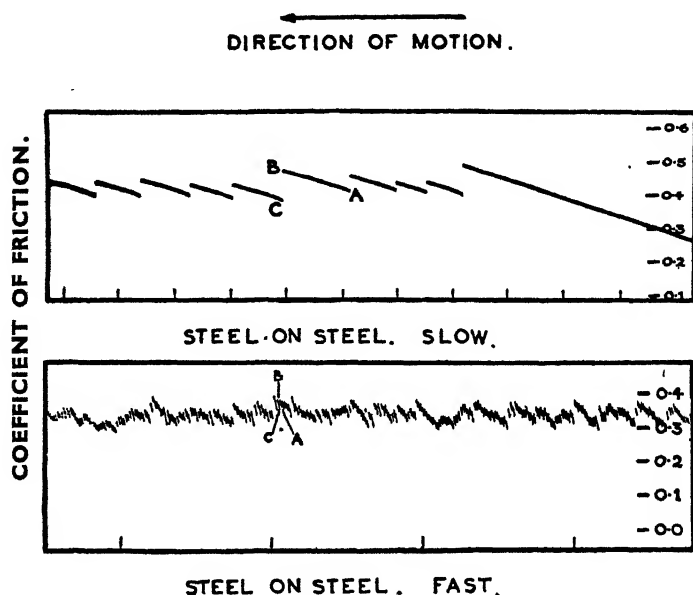
Dr. F. P. Bowden (*Cambridge*) apologised for the omission from the pre-print of the paper issued before the meeting. The approximate composition was given in the final version of the paper as "principally naphthenic and containing two to three per cent. of aromatic compounds."

¹⁰ Bowden and Ridler, *Proc. Camb. Phil. Soc.*, 1935, 31, 431; Bowden and Ridler, *Proc. Roy. Soc., A*, 1936, 154, 640.

¹¹ Bowden and Hughes, *ibid.*, 1937, 160, 575.

He would like to mention that the behaviour was not confined to that particular oil. Other oils such as Pensylvanian Brightstock and mineral oils from other sources showed the same general behaviour, although the temperatures and times required were different.

Williams had asked why the "stick-slips" were so regular; the fact is that they are not absolutely regular. This can be seen when a large number of observations are made. Some typical results for steel on steel are shown in Figs. 1 and 2. AB corresponds to the "stick" and BC to the "slip."



FIGS. 1 and 2.

Fig. 2 includes some hundreds of "stick-slips" and it will be seen that the value of the maximum friction and the extent of the slip both show an appreciable variation.

During the dark part AB of the trace the surfaces are sticking together and the slope is the same throughout because it corresponds to the uniform rate of motion of the lower surface. The intermittent motion is not caused by random scratches on the surface. It appears to be due to the formation of metallic junctions, and the maximum value of the friction corresponds to the maximum strength of these junctions. If the surfaces are carefully prepared and the load and conditions of sliding are constant we might expect this to be reasonably reproducible and hence the stick-slip to be reasonably regular.

PART. II.—CATALYTIC REACTIONS OF HYDROCARBONS.

THE ACTIVATION OF HYDROGEN IN CATALYTIC REACTIONS OF HYDROCARBONS.

By A. FARKAS.

Received 9th February, 1939.

A large group of catalytic reactions of hydrocarbons involves the activation of hydrogen; that is, the breakage and formation of hydrogen-carbon bonds. Research on catalytic reactions of this type covers an enormous field¹ owing to the variety of substances dealt with and to the fertile stimulation which these investigations have received from industrial problems.

Still, even a cursory review of these researches reveals the remarkable fact that most experiments have been performed under rather harsh conditions, in which a great many reactions proceed simultaneously, so that it is difficult to trace the more simple and elementary processes. It is proposed to treat here only the simplest among these reactions, those which do not involve a breakage of carbon-hydrogen bonds. In view of the great variety of catalysts which might induce such reactions, it seems desirable further to restrict this review to those reactions which are catalysed by metals.

1. The Interaction of Hydrogen with the Catalyst.

The simplest case of catalytic activation is that of molecular hydrogen by a metallic catalyst. For a long time it has been suggested that this activation consists of the formation of a layer of atomic hydrogen on the surface of the catalyst, but it was not possible to measure the rate of dissociation and even the experimental evidence supporting this suggestion was rather scarce.

When in 1929 *ortho*- and *para*-hydrogen were discovered by Bonhoeffer and Harteck a closer investigation of the interaction of hydrogen and metallic catalysts became possible. The kinetics of the catalytic *ortho*-*para*-conversion of hydrogen on platinum and other metals² have then actually shown that the conversion can be readily explained by the dissociation of molecular hydrogen on the surface of the catalyst. If hydrogen molecules come into contact with the catalyst they are adsorbed in a state in which the bond between the two atoms in a molecule are loosened to such an extent that the individual atoms are bound more firmly to the metal than to each other. In the process of recombination any atom is able to recombine with any other in its neighbourhood, and in this process *ortho*- and *para*-molecules are formed in a ratio

¹ E.g. Egloff, *The Reactions of Pure Hydrocarbons*, Reinhold Publishing Corporation, New York, 1937.

² Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, p. 89, University Press, Cambridge, 1935.

which corresponds to the temperature of the catalyst and which is independent of the original *ortho-para* ratio of the molecules from which the atoms were formed. Thus, the number of *para*-hydrogen molecules converted by the catalyst is a direct measure for the number of hydrogen molecules dissociated on the surface of the catalyst.

A further test of the proposed mechanism for the *ortho-para*-conversion of hydrogen could be undertaken when deuterium became available for experiments. It could then be shown that on a catalyst all the reactions



proceeded at similar speeds, indicating that in fact all of them proceed according to the same mechanism.^{3, 4, 5} This was an important point for the following reason. In the mechanism of the catalytic conversion of *para*-hydrogen, it was assumed that the dissociation of hydrogen on the surface of the catalyst is the rate-determining step. This assumption is not at all necessarily true, since it is also possible that the rate of conversion is governed by the migration of the atoms in the adsorption layer. If the migration of the atoms be the rate-determining step one would expect the conversion (1) and (2) to proceed faster than the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ since the reunion of two atoms formed from the same molecule should lead to *ortho-para*-conversion, but to no formation of HD molecules. Reaction (3) can only occur if the hydrogen atoms formed primarily migrate to and re-unite with neighbouring atoms. In fact it was found⁵ that the rate of the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ lies between that of the conversion of *para*-hydrogen and that of *ortho*-deuterium. The following figures will give an idea about the rate of dissociation. In the presence of a platinised platinum foil of an area of 2 cm.², 2.9×10^{16} molecules were dissociated per second at 26° C. and 18 mm. hydrogen pressure. The rate of dissociation had an activation energy for light or heavy hydrogen of 10 to 11 k.cals., and the rates of reactions (1), (2) and (3) were in the ratio 1 : 0.54 : 0.67.

Any one of these interactions of hydrogen can be used for measuring the rate of dissociation of hydrogen on any catalyst and also for the estimation of the density of the adsorption layer. If the adsorption layer is saturated, the apparent order of zero will be observed for the conversion reaction whereas in the case of weak adsorption an order about unity will result. In the presence of another reaction partner the displacement of hydrogen will become manifest by a lowering of the rate of *para-ortho*-conversion or of the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$. Thus by varying the concentration of the hydrogen and its reaction partner it is possible to deduce adsorption isotherms for both from the rate of the interchange reactions (1), (2) or (3).

As an example of the use of *para*-hydrogen as research tool the diffusion of hydrogen through palladium⁶ may be mentioned. It was known from earlier experiments that the hydrogen occluded by palladium is present inside the metal in atomic form and that atomic hydrogen produced electrolytically or otherwise is very readily taken up by palladium. By

³ Farkas and Farkas, *Proc. Roy. Soc., A*, 1934, 144, 467.

⁴ Farkas, *Trans. Faraday Soc.*, 1936, 32, 416.

⁵ Farkas and Farkas, *J. Am. Chem. Soc.*, 1938, 60, 22.

⁶ Farkas, *Trans. Faraday Soc.*, 1936, 32, 1667.

simultaneous measurement of the kinetics of the *para*-conversion on and of the diffusion through a palladium disc or tube it was shown that under certain conditions of catalytic activity of the surface of the metal, the same rate-determining step was involved in the diffusion and in the conversion processes. Since, furthermore, it was also shown that this rate-determining step was a surface reaction the conclusion that the rate-determining step was actually the catalytic dissociation of hydrogen molecules was evident.

2. The Catalytic Interaction of Hydrogen and Hydrocarbons.

Until recently there was only one type of reaction which came under this heading, *viz.*, catalytic hydrogenation. In the interchange with heavy hydrogen another type of reaction became apparent leading to an exchange of hydrogen atoms between the hydrocarbons and the hydrogen molecules. These two kinds of reactions will be treated separately.

(a) Catalytic Hydrogenation.

One can distinguish between three types of hydrogenation reactions: the hydrogenation of double bonds, the hydrogenation of treble bonds, and the hydrogenation of aromatic rings. The rates of the hydrogenations belonging to these three different classes vary greatly, and it was generally assumed that each particular class of hydrocarbons was characterised by some kind of specific rate of hydrogenation. Thus, for example, it was held that the hydrogenation of olefines is easier than that of benzene.

The observed rate of hydrogenation is, however, in no way characteristic of the specific rate of hydrogenation unless it is ascertained that the concentrations of the reaction partners in the adsorption layer are comparable in the different experiments. A great number of hydrogenations are carried out in solution. The experiments on the catalytic exchange of hydrogen atoms between molecular deuterium and alcohol ⁷ showed that the alcohol molecules are very strongly adsorbed on the catalyst. Consequently the rate of a hydrogenation carried out in an alcoholic solution will greatly depend on the extent to which the reactants are displaced from the adsorption layer by the alcohol. The accidental presence of small impurities which are liable to poison the catalyst might inhibit the hydrogenation of a particular hydrocarbon containing these impurities. As an example, the thiophene content of not especially purified benzene might be referred to. As the hydrogenation is a surface reaction between the adsorbed molecules of hydrogen and of the unsaturated compound it can proceed at a reasonable speed only if both reactants are present in the adsorption layer at a suitable concentration. In general both hydrogen and unsaturated compounds are readily adsorbed and might displace each other in the adsorption layer. The inhibition of the hydrogenation of ethylene by ethylene is well known.⁸ This inhibition is even more pronounced in the case of acetylene⁹ and, on account of the displacement effect, no hydrogenation can be observed on a platinum catalyst if the pressures of acetylene and hydrogen are equal. If, however, the partial pressure of acetylene is reduced immediately a fast hydrogenation sets in. Another good example for the

⁷ Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 678.

⁸ J. Pease, *Am. Chem. Soc.*, 1923, **45**, 1196.

⁹ Farkas and Farkas, unpublished results.

displacement is the hydrogenation of benzene.¹⁰ The reaction between benzene vapour and hydrogen proceeds very fast on a platinum catalyst, but is reduced considerably if the same catalyst is covered with liquid benzene.

It is of interest that, using a platinised platinum foil as catalyst at room temperature, similar hydrogenation rates can be obtained for ethylene, acetylene and benzene if attention is paid to the concentration of the reactants in the adsorption layer.⁹

The different adsorbabilities of acetylene and ethylene and their compounds offer a ready explanation for the phenomenon known as selective hydrogenation.¹¹ Acetylene compounds take up hydrogen in two stages: first the olefinic compounds are formed and the hydrogenation of these starts only after all of the acetylene compound has been used up. Obviously the acetylene compounds are so strongly adsorbed that the adsorption layer remains covered with them even if the concentration of the acetylene compounds has been greatly reduced.¹² The two steps of hydrogenation might occur at the same speed or at different speeds. Usually the second step is the slower reaction¹³ but the opposite case was observed by Bourguel¹⁴ in the hydrogenation of phenylacetylene, methyl ester of octynoic acid, heptyne and octyne. In these examples of hydrogenation, apparently the adsorption of the acetylene derivatives is so strong on the particular catalyst used that most of the hydrogen is displaced from the adsorption layer.

The second point of discussion relates to the mechanism of catalytic hydrogenation for which processes involving hydrogen molecules, atoms and ions have already been suggested. The addition of molecular hydrogen was proposed as mechanism for the catalytic hydrogenation by Vavon¹⁵ based on the observation that by catalytic hydrogenation of conjugated double bonds no 1-4 addition occurs, whereas usually two atoms are added in 1-4 position if the hydrogenation is carried out by nascent hydrogen. A mechanism involving ionisation of the hydrogen on the surface of the catalyst is advocated by Schmidt.¹⁶

Hydrogenation experiments with *para*-hydrogen reveal a distinct parallelism between the conversion of *para*-hydrogen and the catalytic hydrogenation as shown by the following observations. All hydrogenation catalysts induce the conversion of *para*-hydrogen. On a platinised platinum foil⁵ the temperature dependence of the *para*-hydrogen conversion and of the hydrogenation are equal. The ratio between the *para*-hydrogen conversion and the hydrogenation remains constant, about 4 to 1, at a given temperature even if the absolute activity of the catalyst varies. On the same catalyst the relative rates of hydrogenation by hydrogen and deuterium were about the same as the relative rates for the conversion of *para*-hydrogen and of *ortho*-deuterium. This parallelism indicates sufficiently clearly that the catalytic hydrogenation involves the dissociation of hydrogen molecules on the surface of the catalyst.

The rate of the conversion of *para*-hydrogen in the absence of ethylene gives the maximum rate for the dissociation of hydrogen on the particular catalyst and thus also for the maximum rate of hydrogenation. The

¹⁰ Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 827.

¹¹ Kelber and Schwartz, *Ber.*, 1912, **45**, 1946.

¹² Cf. also Waterman and van Vlodrop, *Rec. trav. chim.*, 1936, **55**, 401.

¹³ Dupont, *Bull. Soc. Chimie France*, 1936 (5), **3**, 1021.

¹⁴ Bourguel, *ibid.*, 1932 (4), **51**, 253.

¹⁵ Vavon, *ibid.*, 1927 (4), **41**, 1235.

¹⁶ Schmidt, *Chem. Rev.*, 1933, **12**, 363.

actual rate of hydrogenation is always smaller than this maximum rate since part of the surface of the catalyst becomes covered with ethylene so that this area is not available for the dissociation of hydrogen molecules. On the mentioned platinised platinum foil,⁵ for example, the following figures were obtained at 27° C.:

Number of hydrogen molecules dissociated per second in the absence of ethylene	1.6×10^{17}
Number of hydrogen molecules added to ethylene per second	3.6×10^{16}
Number of hydrogen molecules recombined per second in the presence of ethylene	2.0×10^{16}

One particular hydrogenation experiment with hydrogen on a nickel catalyst¹⁷ allows us to draw even more detailed conclusions with regard to the mechanism of the hydrogenation. In this experiment hardly any conversion of *para*-hydrogen could be observed, so long as any appreciable amount of ethylene was present. A fast conversion set in, however, immediately the bulk of the ethylene was used up. This result indicates that all hydrogen atoms formed by dissociation of *para*-hydrogen are immediately added to ethylene before they have any chance to recombine to normal hydrogen. The hydrogenation then involves the simultaneous addition of both atoms of the same molecule. It is probable that in certain cases the addition happens so suddenly that the atoms have not yet had sufficient time to travel some distance by diffusion, *i.e.*, the atoms have not yet been completely separated.

This mechanism of catalytic hydrogenation is valid for low temperatures, and agrees with the observation about the catalytic hydrogenation of conjugated double bonds (see above). It is especially supported by the validity of the rules which follow from it with regard to the formation of stereo-chemical isomers in hydrogenations. The suggested mechanism is, however, distinctly different from a mechanism according to which the two hydrogen atoms are added to a double bond independently and in consecutive steps. The latter type of mechanism is operative in hydrogenations by nascent hydrogen and in catalytic hydrogenations at elevated temperatures.

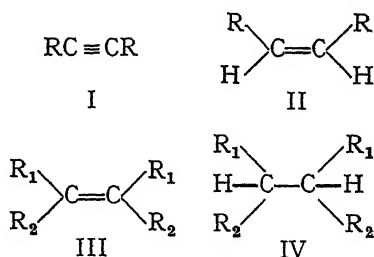
(b) The Formation of Stereo-chemical Isomers in Hydrogenation Reactions.

From the conception of the catalytic hydrogenation as the simultaneous addition of two atoms of the same hydrogen molecule, it follows that the hydrogen atoms will always be added to a double or treble bond in *cis*-position. Consequently the following rules are obtained:¹⁸

1. Acetylene compounds of the type I will give *cis*-ethylene-compounds of the type II.

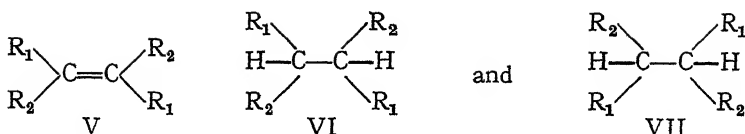
2. *Cis*-ethylene compounds of the type III will give *meso*-compounds of the type IV.

3. *Trans*-ethylene compounds of the type V will give a racemic mixture of the optically active compounds VI and VII.



¹⁷ Farkas, Farkas and Rideal, *Proc. Roy. Soc., A*, 1934, **146**, 630.

¹⁸ Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 837.

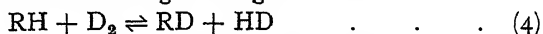


In contradistinction to this scheme, in hydrogenation by nascent hydrogen, or at higher temperatures, the thermodynamically stable isomers will be formed in each case, since then the hydrogenation involves the consecutive addition of two independent hydrogen atoms. The resulting stable isomers are usually the *trans*-compounds if acetylene derivatives are hydrogenated and *meso*-compounds if ethylene derivatives are hydrogenated.

A review of the literature¹⁸ shows that these rules are actually valid in all known cases of hydrogenation in which different stereochemical isomers might be formed. At this occasion the reference to most of the examples must be omitted since they refer to hydrogenation of unsaturated acids or alcohols. The hydrogenation of hydrocarbons has been investigated in the following cases. The catalytic hydrogenation of toluene gives the *cis-trans*-compound, *iso*-stilbene, whereas by the addition of nascent hydrogen the *trans*-compound, stilbene, is obtained.^{11, 19} The catalytic hydrogenation of *cis*- and *trans*-dimethylstilbene produces the *meso*- and the racemic-forms respectively.²⁰ When *ortho*- and *para*-xylene²¹ is hydrogenated at room temperature or slightly higher on a platinum or osmium catalyst mainly *cis*-dimethyl-1, 2-cyclohexane, and *cis*-dimethyl-1, 4-cyclohexane respectively are obtained. On the other hand, from both xylenes the *trans*-compounds result if the hydrogenation is carried out at 180° C. using a nickel catalyst. This result is understandable, since under these conditions the *cis*-dimethylcyclohexanes are transformed into the stable *trans*-compounds. The only apparent exception to the rule is *m*-xylene, since a mixture of *cis*- and *trans*-compounds is obtained even if the catalytic hydrogenation is carried out at low temperatures. A possible explanation for this behaviour is that *cis*-dimethyl-1, 3-cyclohexane is already liable to a *cis-trans* conversion under mild conditions (see below). According to Dupont¹³ the partial hydrogenation of $C_5H_{11}-C\equiv C-CH_3$ on a Raney nickel catalyst yields *cis*-2-octene, and that of $C_5H_{11}-C\equiv C-CH_2-OCH_3$ *cis*-1-methoxy-2-octene. If naphthalene is hydrogenated at low temperature on a platinum catalyst, *cis*-decalin is obtained, whereas *trans*-decalin is formed on a nickel catalyst at 160 to 180° C.^{21a}

(c) Exchange Reactions between Hydrocarbons and Heavy Hydrogen.

The catalytic exchange of hydrogen atoms between hydrocarbons and molecular hydrogen proceeds according to the general formula



where R designates any hydrocarbon radical. The exchange reactions which have so far been investigated are listed in Table I.

¹⁹ Bourguet and Yvon, *Comptes Rend.*, 1936, 182, 224; Ott and Schroeter, *Ber.*, 1927, 60, 624.

²⁰ Ott, *ibid.*, 1928, 61, 2119.

²¹ Chavanne and Becker, *Bull. Soc. Chim. Belg.*, 1922, 31, 95; Miller, *ibid.*, 1935, 44, 513; Zelinsky and Margolis, *Ber.* 1932, 65, 1613; Margolis, *ibid.*, 1936, 69, 1710.

^{21a} Willstaetter and Seitz, *ibid.*, 1924, 57, 684; Hückel, *Ann.*, 1925, 441, 1.

In dealing with exchange reactions one has to establish first of all their relations to other reactions which might accompany them. In the interaction of hydrogen and ethylene or benzene the exchange reaction proceeds simultaneously with the hydrogenation reaction. At room temperature the rate of exchange of ethylene is negligibly slow, but becomes the faster reaction at a higher temperature both on a nickel¹⁷ and on a platinum catalyst.⁵ On platinum the apparent energy of activation for the exchange reaction is 22 k.cals. compared with 10 k.cals. for the hydrogenation. In view of this relatively large difference in the energies of activation the intersection of the curves representing the dependence of the hydrogenation and exchange respectively on temperature indicates clearly that these two reactions proceed according to two entirely different independent mechanisms. The same conclusion must also be drawn from the kinetics of the interaction of benzene and hydrogen.¹⁰ In this case it was found that the absolute rate of the exchange reaction is independent of the hydrogen pressure and proportional approximately to the 0.4th power of the benzene pressure, whereas the absolute rate of the hydrogenation reaction is proportional to the hydrogen pressure but practically independent of the benzene pressure.

The second possibility which has to be considered is what might be termed trivial exchange reactions. Thus, an exchange reaction is necessarily observed if, for example, cyclohexane is brought into contact with heavy hydrogen under conditions under which the dehydrogenation according to $C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$ sets in and leads to the formation of measurable amounts of hydrogen. This was particularly investigated²⁵ and it was found that the decomposition reaction cannot even partially account for the exchange reaction.

TABLE I.—CATALYTIC EXCHANGE REACTIONS OF HYDROCARBONS.

Hydrocarbon.	Catalyst.	Temperature °C.	Pressure in Atm.	Reaction Time.	Reference.
Methane .	{Nickel- Kieselgur }	184-302	ca. 1/2	hours	22
Ethane .	{Nickel- Kieselgur }	110-138	ca. 1/2	"	23
Propane .	{Nickel- Kieselgur }	65-110	ca. 1/2	"	24
Ethylene .	Nickel wire .	58-155	ca. 1/10	minutes	17
" .	Platinum foil .	25-235	ca. 1/10	"	5
Benzene .	{Platinum black, Nickel }	19	ca. 1/4	"	24a
" .	Platinum foil .	17-96	ca. 1/10	"	10
Cyclohexane .	" " .	37-97	ca. 1/10	"	25
n-Hexane .	" " .	55-124	ca. 1/10	"	25

The following mechanism of exchange reaction, which was originally suggested for the first known case of exchange and which will be exemplified in the case of ethylene, seems to explain all cases of exchange reactions very well.

²² Morikawa, Benedict and Taylor, *J. Am. Chem. Soc.*, 1936, 58, 1445.

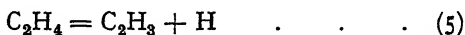
²³ *Ibid.*, 1795.

²⁴ Morikawa, Trenner and Taylor, *ibid.*, 1937, 59, 1103.

^{24(a)} Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, 1934, 30, 663.

²⁵ Farkas and Farkas, *Nature*, 1939, 143, 244; *Trans. Faraday Soc.*, 1939, in this vol., p. 917.

At elevated temperature the bond between the hydrogen and carbon atoms is loosened in ethylene molecules and this loosening of the bond results eventually in dissociation according to a mechanism similar to that operative in the dissociation of hydrogen on a catalyst. It is to be emphasised that this dissociation takes place only on the surface of the catalyst and that only the resulting hydrogen atoms have some mobility whereas the hydrocarbon radicals are firmly held by the catalyst. As the adsorption layer contains heavy hydrogen atoms formed through the dissociation of molecular hydrogen the C_2H_3 -radicals can pick up deuterium atoms when they recombine to ethylene. Thus the mechanism of the exchange can be written as



The rate-determining step in this and in general in other exchange reactions is the dissociation of the hydrocarbon (reaction (5)). The dissociation of the hydrogen molecules (reaction (6)) will govern the rate only in special cases if the surface of the catalyst is completely covered by the hydrocarbon. The relative temperature dependence of the hydrogenation and exchange reaction can then be readily explained by the assumption that the places on the catalyst on which the exchange reaction occurs are not the same as on which the addition of hydrogen happens.

Exactly the same assumption will also explain the dependence of the hydrogenation and of the exchange reaction on the concentration of the reaction partners in the interaction of benzene and heavy hydrogen.

It is quite clear that the same dissociative mechanism of the exchange reaction is capable of explaining the exchange reaction of saturated compounds like methane, ethane, propane, hexane or cyclohexane.

The rate of exchange of any particular hydrocarbon will depend mainly on two different factors: on the loosening of the C—H bond by the catalyst, and on the adsorbability of the hydrocarbon. The present experimental material is insufficient for drawing any general rules. It is possible that there is a certain connection between these two factors if the adsorption of the hydrocarbon on the catalyst is similar to chemisorption and is due to the interaction between the catalyst and the hydrogen atoms of the hydrocarbon.

3. Catalytic Interaction of Hydrocarbons.

The proposed mechanism of the catalytic exchange reactions of hydrocarbon involving the breakage of the hydrogen-carbon bonds might lead to the following reactions, each of which is characterised by a migration of hydrogen atoms.

(a) Exchange of Hydrogen Atoms between Hydrocarbons.

This type of reaction proceeds according to the scheme



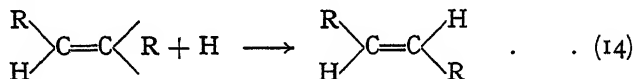
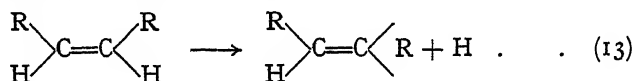
and an example for it was found by Taylor and co-workers²³ in the interchange of hydrogen atoms between light and heavy methane, CH₄ and CD₄, on a nickel catalyst at about 200° C. The progress of the interchange was followed up by means of infra-red spectroscopy. This reaction can be considered as a direct proof for the proposed mechanism of exchange reactions in general.

It is interesting to note that this exchange reaction is faster than the one between CH₄ and D₂. According to the authors this is due to methane molecules being displaced by the hydrogen.

In this connection attention should be drawn also to another effect which might influence exchange reactions in the opposite sense. At low concentrations of the hydrocarbons (RH), the rate-determining step in the exchange is either reaction (9) or (10), whereas at low concentrations of hydrogen the reverse process, the union of the hydrogen atoms with the hydrocarbon radicals, reaction (11) or (12) might govern the rate. Consequently an absence of an interchange reaction between two hydrocarbons, each of which exchanges readily with molecular hydrogen, is no proof against the dissociation mechanism of catalytic exchange reactions.

(b) *Cis-trans* Conversion.

The mechanism for the catalytic *cis-trans* isomerisation of ethylene derivatives for example is as follows: ¹⁸



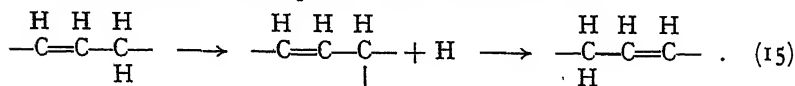
Up to now no cases of catalytic *cis-trans*-conversion of ethylene hydrocarbons (e.g., 2-butene, stilbene) have been observed, although the corresponding thermal reactions have already been studied.²⁶

It might be mentioned that catalytic isomerisation of dimethyl maleate has been repeatedly observed on hydrogenation catalysts.²⁷ On a palladium catalyst the reaction proceeds at 100° C. and the apparent energy of activation is 7 k.cals.²⁸

According to Margolis²¹ *cis*-dimethyl-1, 2 or 1, 4-cyclohexane is transformed on a nickel catalyst at 170° C. to the corresponding *trans*-compounds. This conversion is a suitable example for closer investigation since in this case it is possible to compare the velocity of the isomerisation directly with the velocity of the exchange reaction. Such a comparison is not possible in the case of ethylene compounds on account of the hydrogenation reaction.

(c) Isomerisation by Migration of the Double Bond.

The mechanism of this process can be written thus:



²⁶ Kistiakowsky and Smith, *J. Am. Chem. Soc.*, 1934, **56**, 638; 1936, **58**, 766

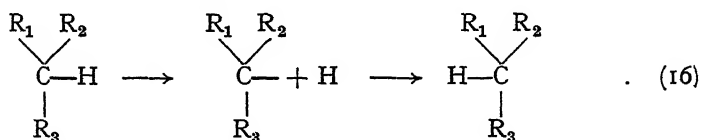
²⁷ Kuhn in Freudenberg's *Stereochemistry*, Leipzig and Wien, 1933, p. 918.

²⁸ Farkas and Reibenbach, unpublished results.

The following examples of this reaction are known: 2, 6 dimethyl-7-octene is transformed into 2, 6 dimethyl-6-octene when passed over a palladium catalyst at 200° C. in a CO₂ stream.²⁹ By the action of palladium black saturated with hydrogen β-pinene is converted into α-pinene at room temperature.³⁰

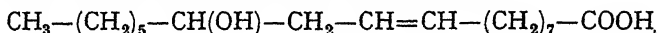
(d) Racemisation of Optically Active Hydrocarbons.

This reaction can be written :



No example for this process is yet known.

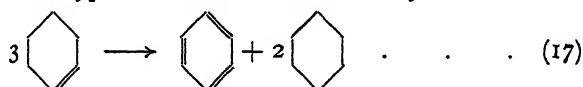
The loss of the optical activity of ricinoleic acid



by catalytic hydrogenation on nickel³¹ might be due to this kind of racemisation occurring on the hydrogenation catalyst.

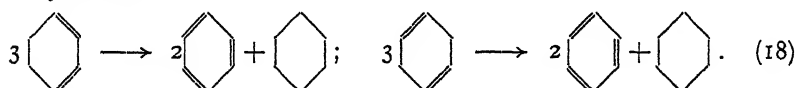
(e) Hydrogenation-dehydrogenation of Cyclo Olefines and Related Compounds. (Disproportionation).

For cyclohexene this type of reaction can summarily be written as

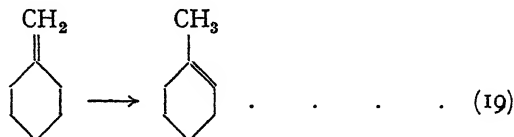


and consists of the transfer of hydrogen atoms from one molecule to another. The position of the equilibrium is such that the reaction proceeds completely in the given direction. The catalytic conversion of cyclohexene to benzene and cyclohexane has been found at room temperature on a palladium catalyst.³²

Analogous reactions take place under similar conditions with 1-3 or 1-4 cyclohexadiene :³³



Methyl-cyclohexene is transformed at 116-118° C. by a palladium to a mixture of toluene and methyl cyclohexane.³⁴ Methylene-cyclohexane reacts similarly and involves probably a wandering of the double bond according to



²⁹ Zelinsky and Levina, *Ber.*, 1929, **62**, 1861.

³⁰ Richter and Wolf, *ibid.*, 1926, **59**, 1733.

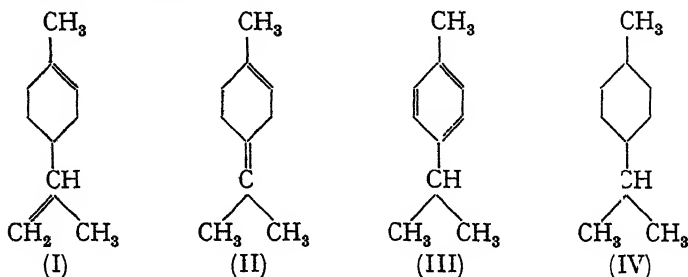
³¹ Walden, *Z. angew. Chemie*, 1925, **38**, 811.

³² Zelinsky, *Ber.*, 1925, **58**, 185.

³³ Zelinsky and Pavlow, *ibid.*, 1933, **66**, 1420.

³⁴ *Ibid.*, 1924, **57**, 1066.

which precedes the disproportionation.³⁵ At 130-160° C. limonene (I) and terpinolene (II) are converted by passage over a palladium catalyst into a mixture of cymene (III) and menthane (IV).^{35, 36}

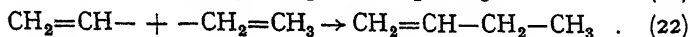
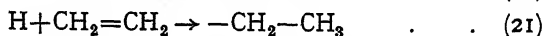
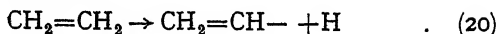


(f) Decomposition-dehydrogenation.

One reaction might come under this heading, namely the catalytic decomposition of acetylene into hydrogen and carbon on contact with catalysts like platinum black, pyrophoric iron, cobalt or nickel.³⁷ This kind of dehydrogenation is to be distinguished from that type of reaction which is the reverse process to hydrogenation.

(g) Polymerisation.

Through the dissociation mechanism the following polymerisation can happen with ethylene, for example :



This process has actually been observed by Taylor and co-workers on a nickel catalyst at room temperature²³ and on a platinum catalyst at 80-100° C.³⁸

Summary.

The catalytic activation of hydrogen molecules involves the formation of atoms on the surface of the catalyst. The rate of dissociation can be measured by the ortho-paraconversion of hydrogen or deuterium or by the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$.

Using these reactions as indicators, valuable information can be derived about the composition of the adsorption layer on the catalyst. It is pointed out that the concentrations of the reaction partners in the adsorption layer are of decisive importance for the rate of interaction between hydrogen and hydrocarbons.

In the catalytic interaction of hydrogen and hydrocarbons hydrogenation and exchange of hydrogen atoms between the hydrocarbon and molecular hydrogen can take place. From catalytic hydrogenation experiments with parahydrogen it follows that the mechanism of hydrogenation involves the simultaneous addition of two hydrogen atoms to a double or treble bond.

³⁵ Zelinsky, *Ber.*, 1924, 57, 2058.

³⁶ Zelinsky and Levina, *ibid.*, 1929, 62, 33.

³⁷ Moissan, *J. Franklin Institute*, 1897, 143, 147; Moissan and Moureau, *Bull. Soc. Chimie France*, 1896 (3), 15, 1296.

³⁸ Farkas and Aman, unpublished results.

This mechanism supplies certain rules for the formation of stereo-chemical isomers in hydrogenation reactions and a review of the literature shows good agreement in all known cases.

The catalytic exchange reaction between molecular hydrogen and hydrocarbons proceeds by a dissociative mechanism according to which the hydrocarbons are partially split into hydrogen atoms and hydrocarbon radicals on the surface of the catalyst. This mechanism offers a ready explanation not only for the kinetics of the exchange reaction of various saturated and unsaturated hydrocarbons but also for the catalytic cis-trans conversion and racemisation of stereo-chemical isomers, for the migration of double bonds, for the disproportionation of cyclohexanes and related compounds and for some polymerisation reactions.

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THE CATALYTIC EXCHANGE OF HYDROGEN ATOMS BETWEEN MOLECULAR DEUTERIUM AND *n*-HEXANE AND CYCLOHEXANE.

BY A. FARKAS AND L. FARKAS.

Received 9th February, 1939.

The catalytic exchange of hydrogen atoms between hydrocarbons and molecular hydrogen has already been investigated in many cases.¹ The present experiments² relate to the exchange reactions of cyclohexane and of hexane, which seem of particular interest as the exchange reactions proceed under rather mild conditions.

Experimental.

The experimental arrangement was the same as that used for the investigation of the interaction of acetone and heavy hydrogen³ and consisted of a reaction vessel containing a platinised platinum foil as catalyst and a glass Foord gauge. The hydrogen and the vapours of hexane or cyclohexane were admitted to the reaction vessel (volume 78 c.c.) through two Bodenstein valves. The deuterium content was determined by the micro-thermal conductivity method. The *n*-hexane and cyclohexane used were spectroscopically pure.

Exchange of Hexane.

A catalytic exchange of hydrogen atoms between chemically pure *n*-hexane and molecular hydrogen was observed previously.⁴ In the present experiments it was ascertained that no incondensable gas was formed even at the highest temperatures used if the hexane was brought into contact with the catalyst. No appreciable decrease in the D-content of the deuterium occurred when the deuterium was admitted alone to the reaction vessel.

¹ Cf., e.g. Farkas, *Trans. Faraday Soc.*, 1939, *in the press*.

² Farkas and Farkas, *Nature*, 1939, 143, 244.

³ Farkas and Farkas, *J. Am. Chem. Soc.*, 1939, *in the press*.

⁴ Farkas and Farkas, *Trans. Faraday Soc.*, 1937, 33, 683.

Fig. 1 indicates the progress of the exchange reaction at 31, 55, 82 and 124° C. The progress of the reaction can be represented by the formula

$$D_t - D = (D_0 - D_\infty)e^{-kt} \quad (1)$$

D_t , D_0 and D_∞ designating the deuterium content in the hydrogen at $t = 0$, t , and in equilibrium respectively. Therefore the rate of exchange

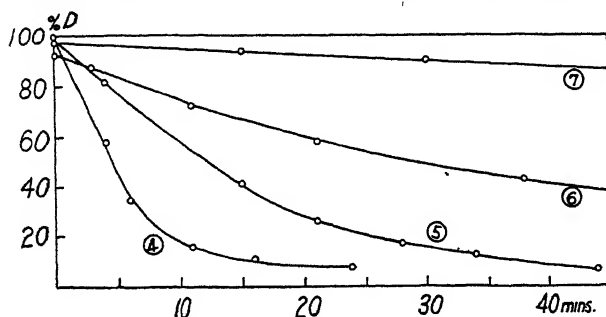


FIG. 1.

Expt. No. 7: 22.5 mm. hexane + 22.5 mm. deuterium at 31° C.

Expt. No. 6: 21 mm. hexane + 21 mm. deuterium at 55° C.

Expt. No. 5: 25.5 mm. hexane + 25.5 mm. deuterium at 82° C.

Expt. No. 4: 26 mm. hexane + 25.5 mm. deuterium at 124° C.

can be characterised by its half-period (τ) as listed in Table I. The apparent energy of activation calculated from the dependence of the half-period on temperature is 9 k.cals. in the temperature region 55-124° C. and is 17 k.cals. at the lower temperature range.

If the hexane is separated from the hydrogen after the exchange has

TABLE I.

No.	Pressures in mm. Hg.		Temperature °C.	Half-Period of Exchange in Minutes.
	C ₆ H ₁₄ .	D ₂ .		
7	22.5	22.5	31	260
6	21	21	55	33
5	25.5	25.5	82	11
4	26	25.5	124	3

taken place and brought together with hydrogen the deuterium content of the hydrogen rises from zero to a value corresponding to the deuterium content of the hexane as shown by the following experiments.

31 mm. hexane and 62 mm. deuterium (containing 98 per cent. D) were equilibrated at

75° C. As the deuterium content of the hydrogen decreased to 14 per cent. the deuterium content of the hexane could be calculated to 24 per cent. These figures correspond to the distribution ratio $(H/D)_{\text{hydrogen}} \cdot (D/H)_{\text{hexane}} = 1.94$. 28 mm. of the deuterated hexane was then brought into contact with 13 mm. hydrogen and after nineteen minutes 12 per cent. deuterium was found in the hydrogen.

The simplest mechanism for the exchange reaction of hexane is the one which has been suggested for the exchange of ethylene⁵ and benzene.⁶ According to this mechanism the hydrocarbon molecules dissociate into hydrogen atoms and radicals on the surface of the catalyst and the exchange takes place as the hydrocarbon radicals recombine with deuterium atoms formed by the dissociation of deuterium molecules. It should be pointed

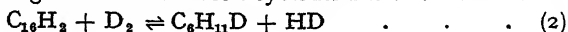
⁵ Farkas, Farkas and Rideal, *Proc. Roy. Soc., A*, 1934, 146, 630; Farkas and Farkas, *J. Am. Chem. Soc.*, 1938, 60, 22.

⁶ Farkas and Farkas, *Trans. Faraday Soc.*, 1937, 33, 827.

out that the exchange reactions of *n*-hexane is not accompanied by any other chemical change. The decrease of the apparent energy of activation at higher temperatures is probably due to the desorption of hexane.

Exchange of Cyclohexane.

The catalytic exchange reaction between cyclohexane and deuterium ⁴



was measured in the temperature range 15-98° C. at pressures of 10-100 mm. Hg and the obtained half-periods are listed in Table II. At 98° C. the half-period is independent of the pressure. The dependence of the rate of exchange of cyclohexane corresponds completely with that found for hexane. It is interesting to note that even the absolute values of the half-periods for the same temperature agree.

TABLE II.

No.	Pressures in mm. Hg.		Temperature °C.	Half-Period of Exchange.
	C ₆ H ₁₂ .	D ₂ .		
17	34	41	15	51 hours.
18	31	31	37	120 mins.
16	45.5	41	65	23 "
19	36	36	98	9 "
20	11	11	98	8.5 "
21	5	5	98	9.3 "

Dehydrogenation of Cyclohexane.

Since the catalytic dehydrogenation of cyclohexane according to



would lead necessarily to an exchange reaction, in additional experiments the position and rate of establishment of this equilibrium was investigated in order to ascertain its possible rôle in or contribution to the exchange reaction.

The establishment of the equilibrium $C_6H_{12} = C_6H_6 + 3H_2$ was followed up by pressure measurements at temperatures from 140° to 202° C. As soon as equilibrium was established the hydrogen formed in the reaction vessel was collected and its volume determined. From the amount of cyclohexane initially admitted and the amount of hydrogen formed, the equilibrium constants were calculated.

In Table III the equilibrium constants and some reaction rates are listed for the temperature range 99-202° C. These equilibrium constants are in agreement with those calculated from the formula

$$\log K_p = -51500/4.573T + 20.69$$

$$K_p = (C_6H_6)(H_2)^3/(C_6H_{12})$$

given by Schultze.⁷ It will be recognised that the rate of the establishment of the dehydrogenation equilibrium is about the same at 140 and 202° C. These results indicate that the hydrogenation reaction



is independent of the temperature and the rate of the dehydrogenation reaction



varies with temperature in a similar way as the equilibrium constant.

The contribution of the hydrogenation-dehydrogenation equilibrium to the exchange reaction is given by the initial absolute rate of the dehydro-

⁷ Schultze, *Z. angew. Chemie*, 1936, 49, 268.

generation reaction and will be of the order of magnitude $V_{\text{equ.}}/2\tau_{\text{equ.}}$, where $V_{\text{equ.}}$ represents the amount of hydrogen present in equilibrium and $\tau_{\text{equ.}}$ the half-period of the establishment of the equilibrium. A direct comparison of the rate of dehydrogenation with the rate of exchange reaction was only possible in the low temperature range.

TABLE III.—THE EQUILIBRIUM $\text{C}_6\text{H}_{12} = \text{C}_6\text{H}_6 + 3\text{H}_2$.

No.	Temperature °C.	Half-Period in Minutes.	$-\log K_p$ Observed.	$-\log K_p$ Calculated.
I	99	—	9.78	9.58
3	120	—	8.47	7.97
5	140	10	6.92	6.58
II	193	—	3.89	3.48
6	202	8.5	3.46	3.02

Table IV gives the results of such a comparison at 97 and 127° C. In the two series of experiments the catalyst used was not in the same state of activity. As a measure for the initial rate of exchange the expression $V_{\text{ex.}}/2\tau_{\text{ex.}}$ was taken, $V_{\text{ex.}}$ representing the absolute amount of deuterium participating in the exchange and $\tau_{\text{ex.}}$ the half-period of the exchange.

TABLE IV.

No.	Temperature °C.	Initial Rate of Dehydrogenation in c.c. min. ⁻¹ .	Initial Rate of Exchange in c.c. min. ⁻¹ .	Ratio: Exchange/Dehydrog.
14, 15	97	0.004	0.19	47
25-27	127	0.028	0.24	8.5

It will be recognised that the absolute rate of dehydrogenation is so small that its contribution to the exchange reaction can be neglected especially at lower temperatures.

As mechanism for the exchange reaction of cyclohexane again the dissociation process



is suggested. It is possible that at a higher temperature, at which the dehydrogenation starts, this process is followed by further dehydrogenation to benzene. It should be noted, however, that then the step (6) proceeds relatively fast and the rate-determining step is the subsequent process.

Finally it might be mentioned that these exchange reactions can be used as a suitable method for preparing deuterated hexane or cyclohexane, and for determining their deuterium content.

Summary.

On a platinised platinum foil, a catalytic exchange of hydrogen atoms between molecular hydrogen and *n*-hexane or cyclohexane takes place. It is shown that in the case of cyclohexane the establishment of the



cannot account for the rate of exchange. It is suggested that in the exchange of both hydrocarbons involves the dissociation of the hydrocarbons into hydrogen atoms and radicals on the surface of the catalyst.

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FUNDAMENTALS IN THE CATALYTIC RING CLOSURE OF OPEN CHAIN HYDROCARBONS.

BY HUGH S. TAYLOR AND JOHN TURKEVICH.

Received 16th February, 1939.

Much of the chemical development of the last fifty years, especially in the field of dyestuffs, drugs, flavours, perfumes, photographic developers and explosives, arose from the fact that certain aromatic hydrocarbons and phenols could be readily obtained from coal tar. The coal-tar industry may be regarded as a by-product of the steel industry, the demand for metallurgical coke making possible a plentiful supply of tar. For this reason, the organic chemist has displayed singularly little interest in alternative methods of producing aromatic and other ring structures from other raw materials, and his interest in the transition from aliphatic to aromatic compounds has been largely pedagogical. Recently, however, the problem has assumed an entirely different aspect owing to the contrast in fuel values of the aliphatic and aromatic hydrocarbons. The superiority of the latter in anti-knock characteristics and the much increased demand, especially for high-grade aviation fuels, the low rating of many of the hydrocarbons to be found in petroleum fractions, cracked or straight distillate, have compelled the consideration of methods of reforming such fractions and have led to significant developments in the techniques of ring closure.

The organic textbook hitherto has contented itself with such statements of the problem as "The preparation of aromatic hydrocarbons from aliphatic compounds is possible but, with a few exceptions, rarely employed."¹ Pyrolysis of the hydrocarbons, acetylene and methane, is known to yield benzene. The action of sulphuric acid on ketones yields aromatic hydrocarbons as, for example, in the conversion of acetone to 1, 3, 5 trimethyl benzene. Ring closure by the action of metals on dihalides, of cyclic ketones by heating calcium salts of the corresponding dibasic acids, special Grignard reactions and malonic ester syntheses are all known. These methods may be characterised as methods of synthesis of fine chemicals. For the bulk production of aromatic compounds from open-chain raw materials in industry it is obvious that use must be made of the materials available in suitable naphtha cuts from petroleum sources, in the light oils, largely paraffinic in nature, arising from the low temperature distillation of coals and in the corresponding fractions of light spirit arising from the high pressure hydrogenation of coal or from the synthetic processes of liquid hydrocarbons starting from water gas with catalysts such as cobalt, iron and nickel. In this latter case it is well known that the product is aliphatic in nature and relatively simple in composition the normal saturated hydrocarbons constituting an important fraction together with simple olefinic hydrocarbons under certain experimental conditions.

¹ J. B. Conant, *The Chemistry of Organic Compounds*, Macmillan, New York, 1934, p. 359.

Conditions Governing the Direction of Change.

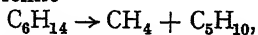
Qualitative indications of the conditions under which the transformation of aliphatic to aromatic hydrocarbons could be achieved are available from the known data of coal distillation and the cracking of petroleum. A comparison of the tar distillates obtained in the low temperature distillation of coal with those obtained in the high temperature processes prevailing in town's gas manufacture and the coke-oven industry indicates that low temperatures favour the formation of paraffinic tars while the aromatics accumulate under the dehydrogenating conditions of the high temperature carbonisation processes. The same conclusion is reached from an analysis of the experience early obtained in the vapour phase cracking of petroleum oils. As an example we may cite the data obtained by Rittmann, in 1914, indicating that, as the temperature was increased at moderate working pressures, yields of aromatics representing 8 per cent. of the oil input could be achieved in one passage through the cracking unit.² As is well known these investigations were made the basis of industrial operations to produce aromatic hydrocarbons during the World War.

The quantitative analysis of the conditions for ring closure and the formation of aromatic hydrocarbons can be based upon a thermodynamic analysis of the hydrocarbons concerned and the several types of reaction which they may undergo. This analysis has been enormously facilitated by recently accumulated fundamental data so that it is now possible to set forth a fairly comprehensive picture of the many equilibria involved and their controlling factors of temperature and pressure. This is done in the succeeding section. Here we wish only to emphasise, in anticipation of the conclusions set forth below, that the known stability of the benzene ring, now interpreted as due to a resonance energy of 39.4 k.cals.,³ provides a factor of available energy in the transformations of aliphatic to aromatic structure, which changes an unfavourable equilibrium picture in the systems, saturated aliphatic, corresponding olefine, hydrogen, to one in which the equilibrium between aliphatic hydrocarbon, hydrogen and aromatic is displaced almost quantitatively in favour of the aromatic hydrocarbons at temperatures where side-reactions may be largely suppressed provided suitable catalysts for the ring closure can be secured.

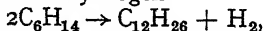
Thermodynamic Approach.

The thermal decomposition of paraffin hydrocarbons is a complex process since it may be considered as taking place along one or more of the following lines. Thus, hexane may decompose to form

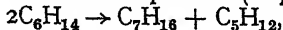
- (1) a paraffin and olefine



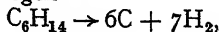
- (2) a higher paraffin and hydrogen



- (3) a higher paraffin and a lower paraffin (disproportionation)



- (4) carbon and hydrogen



² *Ind. Eng. Chem.*, 1916, 8, 350-361.

³ Gilman, *Organic Chemistry*, Wiley, New York, 1938, p. 1874.

- (5) olefine and hydrogen

$$\text{C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_{12} + \text{H}_2,$$
- (6) cycloparaffin and hydrogen

$$\text{C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_{12} + \text{H}_2,$$

$$\text{C}_6\text{H}_{14} \rightarrow \text{C}_5\text{H}_9 \cdot \text{CH}_3 + \text{H}_2,$$
- (7) cyclo olefine and hydrogen

$$\text{C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_{10} + 2\text{H}_2,$$
- (8) aromatic and hydrogen

$$\text{C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_6 + 4\text{H}_2.$$

The above equations are the more simple types of decomposition reactions. Their list may be extended by considering the interactions of the original paraffin hydrocarbon with its decomposition products: hydrogen, paraffins, olefines, naphthenes and aromatics.

This complex picture of hydrocarbon transformations may be clarified to a certain extent by the use of thermodynamic characteristics of the individual reactions. Free energy data on hydrocarbons are rapidly accumulating. While these data are not sufficiently accurate to give a precise picture of the equilibrium characteristics of hydrocarbon reactions, they may serve to orient one in the maze of conceivable reactions and express in a succinct way the possibility of various reactions at different temperature intervals.

With that object in mind, linear free energy equations were derived for the most part from the data collected by Thomas, Egloff and Morrell,⁴ checked by the recent thermal data of Kistiakowsky.⁴ The standard free energy of formation from graphite and hydrogen at one atmosphere pressure in the temperature range 300-1000° K. is given by the following approximate equations:

Methane $\Delta F_T^\circ = -19,050 + 22.6T.$

Normal paraffins with n carbon atoms

$$\Delta F_T^\circ = -10,550 - 5.890n + 25.2nT - 2.2T \quad (n > 1).$$

Ethylene $\Delta F_T^\circ = 10,770 + 16.9T.$

Olefines with double bond in the terminal position and n carbon atoms

$$\Delta F_T^\circ = 20,321 - 5.835n - 33.26T + 24.52nT. \quad (n > 2).$$

Cyclohexane $\Delta F_T^\circ = -32,000 + 135.5T.$

Methyl cyclopentane $\Delta F_T^\circ = -22,600 + 88.2T.$

Cyclohexene $\Delta F_T^\circ = -3,300 + 104.1T.$

Cyclohexadiene $\Delta F_T^\circ = 23,470 + 72.9T.$

Benzene $\Delta F_T^\circ = 17,900 + 41.7T.$

The standard free energy change accompanying various reactions was determined by appropriate additions and subtractions. From the experimental point of view one is interested primarily in the degree of dissociation of the hydrocarbon along a given reaction path. Free energy values for various reactions give a distorted measure of the extent of decomposition because of the complicated relationship between the standard free energy value and equilibrium constant on the one hand and the equilibrium constant and fraction dissociated on the other. Because of this fact, calculations were made to determine, as a function of temperature, the extent of decomposition of hexane, in mole per cent. at one atmosphere pressure according to the various reaction paths.

⁴ *Ind. Eng. Chem.*, 1937, 28, 4260.

Because of the uncertainty in the free energy data, the results are not very accurate. They do, however, give a schematic picture of the thermodynamic implications of the various reaction paths.

Fig. 1 represents the mole per cent. of decomposition of *n*-hexane according to various reactions, as a function of the absolute temperature. The following conclusions can be drawn:

(1) Two paraffin molecules cannot form a higher paraffin by the elimination of a molecule of hydrogen. This conclusion is in accord with the experimental fact that the reverse reaction (destructive hydrogenation) can be realised. In the catalytic hydrogenation of petroleum a paraffin is cracked and hydrogenated to lower paraffins. Polymerisation of paraffins with the elimination of hydrogen is ruled out on the thermodynamic basis.

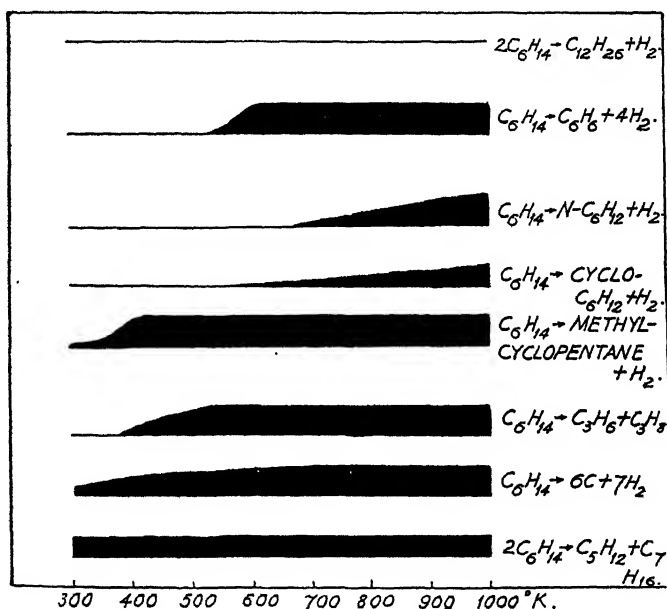


FIG. 1.—Decomposition of hexane into various reaction products as a function of temperature. (The ordinates of the individual graphs represent the mole per cent. of products arising from the decomposition of 1 mole of heptane at constant pressure of 1 atmosphere.)

(2) Cyclisation of hexane to benzene sets in about 500° K. and the equilibrium at one atmosphere pressure is completely on the side of benzene at about 600° K.

(3) The dehydrogenation of hexane to olefine and cyclohexane does not become appreciable below 800° K. The dehydrogenation of hexane to methyl cyclopentane sets in at the surprisingly low temperature of about 350° K. Great weight cannot be attached at present to this result since the free energy data on methyl cyclopentane are by far the least accurate of all the data. The three above dehydrogenation reactions are not serious competitors to cyclisation to aromatics since their products, olefines and six-membered cycloparaffins, are thermodynamically unstable with respect to aromatics above 550° K. They thus may serve in the above temperature region as intermediate reactions.

(4) The cracking to olefine and lower paraffins, the decomposition to carbon and hydrogen, the disproportionation to a lower and higher paraffin, are all appreciable in the same temperature region in which cyclisation of the paraffin to aromatic takes place. These reactions are

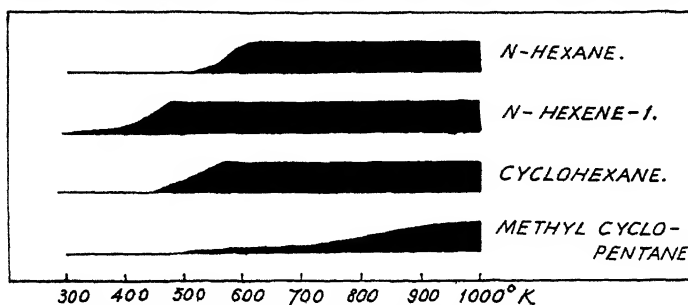


FIG. 2.—Formation of aromatics from various hydrocarbons as a function of temperature. (The ordinates of the individual graphs represent the mole per cent. of aromatics produced by 1 mole of the various hydrocarbons at constant pressure of 1 atmosphere.)

thermodynamically serious competitors to aromatisation, and are all characterised by the fact that a carbon-carbon bond must be broken. The choice of alternative paths, cracking or aromatisation, cannot be affected by shift of temperature, but must be carried out by proper choice of catalysts.

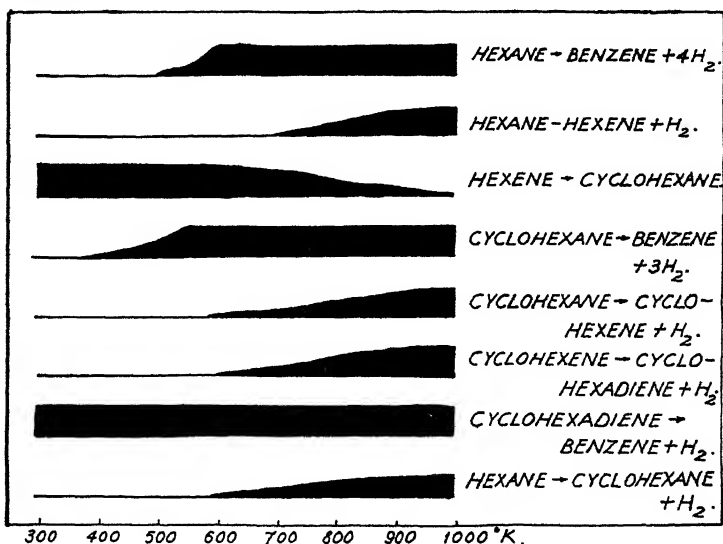


FIG. 3.—Decomposition of intermediates as a function of temperature. (The ordinates of the individual graphs represent the mole per cent. of the products arising from 1 mole of reactant at constant pressure of 1 atmosphere.)

Fig. 2 represents the yield of aromatics in mole per cent. from various hydrocarbons. It is readily seen that aromatic hydrocarbons are the more stable form at elevated temperatures. This fact may be correlated with the existence of a conjugated double bond system in benzene which confers on the latter a marked stability due to resonance energy.

Fig. 3 represents as a function of temperature the yield of various intermediates in the conversion of hexane to benzene. It is readily seen by examination of the diagram that, at 750°K. , the temperature at which the aromatisation is realised experimentally, the steps more difficult from the thermodynamic point of view are the elimination of a molecule of hydrogen from hexane, cyclohexane and cyclohexene. The rearrangement of hexene to cyclohexane and especially the conversion of cyclohexadiene to benzene are predominantly favoured. It is the high stability of the aromatic which compensates for the unfavourable equilibrium relationships of some of the intermediate steps. Thermodynamics however furnishes no criteria for differentiating between various alternative mechanisms for the overall processes: hexane to benzene and hydrogen.

All the calculations presented were those calculated for the six carbon molecules. These were chosen because better thermodynamic data are available for this class of hydrocarbons than for others. Available thermal data on other than six carbon atom compounds give essentially the same thermodynamic picture.

The main conclusions to be drawn from thermodynamic considerations are that one should operate at temperatures above 300°C. if one is to obtain a dehydrogenation of paraffin hydrocarbon to an aromatic, that one should deal with catalysts that activate the carbon hydrogen bond and avoid all substances which rupture the carbon-carbon bond.

The Catalyst Problem.

The processes involved in ring closure of paraffins and olefines are all processes of dehydrogenation and the catalysts determining the production of aromatics must be sought in that large body of catalysts known for their efficiency of dehydrogenation. This includes the metal catalysts such as Fe, Ni, and Co, the platinum metals and Cu and, in addition, a considerable body of oxide catalysts which have been added to the general list of hydrogenation-dehydrogenation catalysts.

Data accumulated in the Princeton laboratories over a considerable number of years indicate quite definitely that it would be among the oxide catalysts of dehydrogenation that the catalysts of aromatisation would be found. The metals Ni, Co, Fe would be of doubtful utility because of the known tendency of these metals to break C—C bonds with formation of metallic carbides, carbon and lower hydrocarbon fission products. Investigations on the capacity of nickel⁵ and of cobalt⁶ to break C—C bonds in ethane and propane have revealed that the hydrogenation-decomposition of even these lower aliphatics is marked at 200°C. Metallic Cu, which manifests a marked inertness to fission of the C—C bond, suffers from the well-known disadvantage that in the neighbourhood of 400°C. it suffers rapid deterioration in activity due to processes of sintering. Certain of the platinum metals reveal activity similar to Ni in C—C bond fissure, with Pt as among the less active in this regard. Apart from economic factors, however, it is in the lower ranges of temperature that these catalysts have exercised pronounced dehydrogenating efficiency.

It is characteristic of the hydrogenation-dehydrogenation oxide

⁵ *J. Amer. Chem. Soc.*, 1936, **58**, 1795; 1937, **59**, 1103.

⁶ E. H. Taylor, *Thesis*, Princeton, 1938; *J. Amer. Chem. Soc.*, 1939, **61**, 503.

catalysts as a group that they exercise their activity in a higher temperature range than is required by the metals. This is revealed not only by actual catalytic data but also by the data on activated adsorption of hydrogen by these oxides. It is only above room temperatures where these adsorptions become marked whereas the metals display such adsorption at liquid air temperatures. Zinc and manganese oxides were measured for hydrogen adsorption between 56 and 400° C., zinc and manganese chromites from room temperature upwards, Cr_2O_3 gel from 110° to 400° C., and, to take extreme cases, those of SiO_2 and Al_2O_3 , the activated adsorption of hydrogen on these oxides begins to be measurable at 400° C. and upwards.⁷

The activity of oxides in the hydrogenation-dehydrogenation reactions of hydrocarbons was definitely indicated in the researches of Lazier and Vaughen⁸ who studied their efficiency in the hydrogenation of ethylene. Their claim of a unique position for Cr_2O_3 catalysts was shown to be only one of degree by the researches of Turkevich⁹ and of Howard¹⁰ on the activated adsorption of hydrocarbons by manganese chromite and chromium oxide gel. These latter researches indicated that the activated adsorption of saturated paraffins was negligible on the oxide catalysts below 300° C. but that at higher temperatures there was definite evidence of interaction between these gases and the surface leading to fissions in the adsorbed molecule.

The conversion of a paraffin hydrocarbon to an aromatic hydrocarbon with the elimination of hydrogen was considered to involve the following steps:

- (1) Activated adsorption of the paraffin on to the surface.
- (2) Surface dehydrogenation with the formation of adsorbed aromatic and adsorbed hydrogen.
- (3) Desorption of the hydrogen.
- (4) Desorption of the aromatic.

The rate of the catalytic conversion of heptane to toluene will be that of the slowest of these steps. The oxide catalysts, principally chromium oxide, were ideally suited for catalysts in aromatisation. Previous researches showed that activated adsorption of paraffins took place readily on these surfaces above 300° C. and resulted in the rupture of the C—H bond. These oxide catalysts would lead to little cracking of C—C bonds. Furthermore, at about 450° C., in the case of Cr_2O_3 , hydrogen is being readily desorbed. The paraffin could therefore compete on an equal basis with the hydrogen for the surface. Thus the accumulation of hydrogen on the surface would not unduly poison the reaction.

There are no data on the relative adsorption of aromatics and paraffins. It was felt, however, that if the paraffins could compete effectively for the surface with hydrogen, a substance which has a strong affinity for hydrogenating-dehydrogenating catalysts, the paraffin would also compete with the aromatic hydrocarbon.

The above considerations led logically to a study of the interaction between the higher hydrocarbons and oxide catalysts, principally Cr_2O_3 gel, a study which has been in progress steadily over a period of years,

⁷ J. Amer. Chem. Soc., 1931, **53**, 813, 2168; 1932, **54**, 602; 1934, **56**, 586, 1685; Z. physik. Chem. (Bodenstein Festband), 1931, 475.

⁸ Lazier and Vaughen, J. Amer. Chem. Soc., 1932, **54**, 3080.

⁹ Turkevich and Taylor, *ibid.*, 1934, **56**, 2254.

¹⁰ Howard and Taylor, *ibid.*, 2259.

some of the data of which, demonstrating both dehydrogenation and ring closure will be presented below.

Publication of data on aromatisation of saturated and olefinic hydrocarbons when passed over Cr_2O_3 was made by Moldavskii, Livschitz and Kamusher in 1936.^{11,12} In addition to Cr_2O_3 other dehydrogenation catalysts, for instance, molybdenum sulphide and activated carbon were found to produce cyclisation and ZnO , Al_2O_3 , ThO_2 , NiCrO_4 , UO_3 , and floridin were tried. On Cr_2O_3 normal octane was converted at 460°C . into a product containing 63 per cent. aromatics, especially *o*-xylene. It was also shown that 2,5 dimethyl hexane and heptane also yielded aromatics under similar conditions. Shortly thereafter Kazanski and Plate¹³

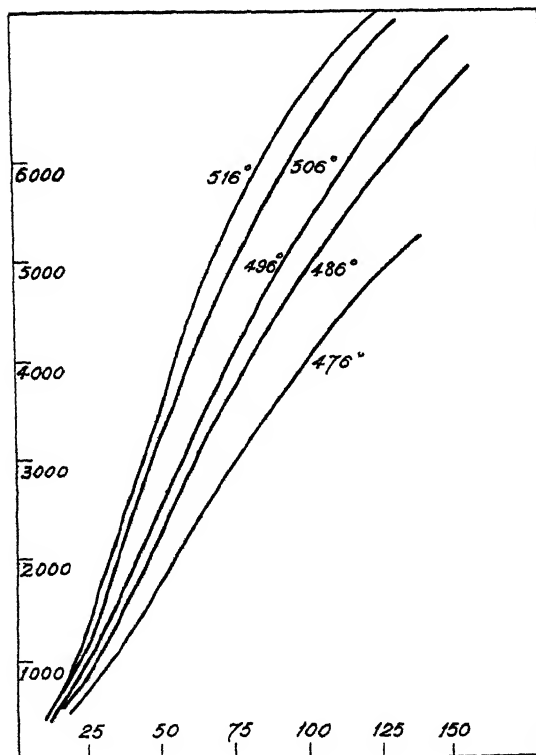


FIG. 4.—The temperature variation of gas evolution from heptane on chromium oxide. (The ordinates are cubic centimeters of gas evolved. The abscissæ are minutes.)

noted that on charcoal containing 25 per cent. Pt at $300\text{--}315^\circ\text{C}$. not only butyl and amyl cyclo-pentanes but also di-isobutyl, normal octane and di-isoamyl were converted partially into aromatics especially, in the case of the latter three, in absence of hydrogen as carrier gas.

The data of Moldavski, Kamusher, and Kobyl'skaya¹⁴ amplify the earlier results. In this work they report that glass and silica gel appear to be inactive, while ZnO , TiO_2 , Mo_2O_3 , and MoS_2 , activated carbon, and carbon from pyrolytic treatment of hydrocarbons were able to cause

¹¹ *Comptes rendus, U.S.S.R.*, 1936, 10, 343.

¹² *J. Gen. Chem.*, 1937, 7, 169.

¹³ Kazanski and Plate, *Ber.*, 1936, 69, 1862.

¹⁴ *J. Gen. Chem., U.S.S.R.*, 1937, 7, 1835, 1840.

aromatisation of normal octane. With TiO_2 a yield of 27 per cent. aromatics and with MoS_2 one of 35 per cent. are recorded but yields of 4 and < 2 per cent. were obtained with ZnO and Mo_2O_3 . These authors also call attention to literature indicating that the catalytic cracking of higher hydrocarbons can yield either complex aromatics which lose side chains by the cracking process or form fragments which aromatise. Gault and Sigwait¹⁵ report this phenomenon in the cracking of hexadecane at 450° over Ni on pumice with a fraction condensing below 200° containing 50 per cent. aromatics and a gas yield with 86.5 per cent. hydrogen. Kharzhev, Sever'yanova, and Siova¹⁶ treated normal decane over chromium-copper-phosphorus catalyst at 500° and found 45 per cent. aromatic hydrocarbons in the product. Borisov and Gaverdovskaya¹⁷ noted the aromatisation of kerosene when cracked on oxides of uranium, titanium, and thorium.

A number of earlier patents definitely indicate the activity of oxides in the dehydrogenation of hydrocarbons. Thus, the patents to Mittasch, Pier, Wietzel, and Langheinreich¹⁸ U.S.P. No. 1,913,940 and its divisional application 1,913,941 relate to the use of oxides of the metals of the sixth group alone or in admixture with other materials, notably active carbon. They are concerned with "the production of valuable, chiefly aromatic hydrocarbons from low boiling aliphatic hydrocarbons and hydroaromatic hydrocarbons of any origin." A patent to Pier and Donath¹⁹ covers dehydrogenation of benzine with metals of Groups V, VI and VII with metalloids or oxides of the fifth group, as well as Pb, Sn, Zn, Cd or their compounds as additional substances. The patent to Wietzel and Pfaundler²⁰ discloses the production of aromatic hydrocarbons, in contact with Mo, W, Cu, ferrosilicon, ZnO , Mo_2O_3 , Cr_2O_3 , ThO_2 , CeO_2 , copper borate, active charcoal, active silica and aluminium borate, from the liquid hydrocarbons obtained by polymerisation of gaseous olefines.

Two patents to Frey and Huppke²¹ cover dehydrogenation of hydrocarbons with a dark vitreous chromium oxide gel and with such a gel containing difficultly reducible oxides of Al, Zr, Ti, Si, Th, Bo, and Mg, in intimate association with the hydrous chromium oxide. Neither of these patents discusses the dehydrogenation which results in the formation of aromatic hydrocarbons. Our own researches in Princeton, with heptane as raw material reveal that certain vitreous gels, promote ready conversion to toluene with negligible amounts of side reactions. Some of the Princeton data, as well as our survey of other starting materials and catalysts are set forth in the succeeding sections to illustrate the generality of the cyclisation phenomena with open chain saturated and unsaturated materials.

Quite recently a series of patents issued to Morrell and to Grosse of the Universal Oil Products Company,²² seeks to protect the use of compounds of Cr, Mo, W, U in Group VI, V, Cb, Ta in Group V, and Ti, Zr, Ce, Hf, Th in Group IV, with and without admixed oxides and support materials.

¹⁵ *Ann. Comb. Liquides*, 1927, 2, 543.

¹⁶ *Khimia Tverdogo Topliva*, 1936, 7, 559.

¹⁷ Borisov and Gaverdovskaya, *Neftyanoe Khozyaistvo*, 1934, 26, 10, 27.

¹⁸ June, 1933; Conv. Date, February, 1926.

¹⁹ U.S.P. No. 1,975,476; Conv. Date, December, 1929.

²⁰ U.S.P. No. 1,910,910, May, 1933; Conv. Date, November, 1925.

²¹ U.S.P. No. 1,905,383, July, 1930. Issued April, 1933. U.S.P. No. 2,098,959, May, 1934. Issued, November, 1937.

²² U.S.P. Nos. 2,124,566; 2,124,567; 2,124,583; 2,124,584; 2,124,585; 2,124,586 of September-October, 1936. Issued July, 1938.

Still more recently, Koch²³ has reported that appropriate fractions of synthetic gasoline obtained from water gas can be aromatised on vanadium oxide and chromium oxide catalysts supported on alumina.

Experimental Data.

In the following paragraphs is presented a resumé of a large series of investigations carried out over a period of years designed to reveal the fundamental aspects of the catalytic dehydrogenation and aromatisation of open chain hydrocarbons both saturated and olefinic. The majority of the experiments have been carried out on catalysts of Cr_2O_3 in various gel forms with and without addition agents to stabilise the same. This choice was dictated by the large amount of fundamental data obtained in this laboratory on the adsorption characteristics of the catalyst which suggested it as the first material to be studied by us.

Aromatisation of Heptane on Chromic Oxide Gel.—On gels prepared by slow precipitation with ammonia from dilute $\text{Cr}(\text{NO}_3)_3$ solutions²⁴ it is possible to secure essentially quantitative conversion of heptane to toluene in a single passage at slow rates of passage of heptane vapour. This is shown to be possible at temperatures of 470°C . in Table I. Data there given show that, with decrease of contact time, conversion is no longer

TABLE I.—AROMATISATION OF *n*-HEPTANE ON CHROMIUM OXIDE GEL, ON THORIA AND ON ALUMINA.

Catalyst.	Temp. °C.	Liquid Flow cc./hr. / 15 g. of Catalyst.	Mols. Gas Per Mol. C_7H_{16} .	Gas Com- position Per Cent H_2 .	Liquid Product in Per Cent.		
					Aromatic.	Olefines.	Saturated.
Cr_2O_3	468	3	3.75	95	100	0	0
Cr_2O_3	468	9	3.77	94	100	0	0
Cr_2O_3	468	18	3.03	92	92.3	1.8	5.9
Cr_2O_3	468	27	2.75	98	69	6	25
ThO_2	468	3	0.05	1	0	0.5	99.5
Al_2O_3 (gel)	540	3	0.05	4	0	0.3	99.7
Al_2O_3 (activated)	540	3	0.4	42	2	16.0	82

complete but the process occurring is essentially unchanged. To differentiate the activity of the gel from other catalysts, experiments carried out under similar conditions of vapour flow with ThO_2 on pumice from $\text{Th}(\text{NO}_3)_4$ on an alumina gel and on a technical, but high grade, activated alumina are also given.

On the basis of the hydrogen yield the slowest rates of passage correspond to 89 per cent. conversion to toluene. Actually the liquid obtained analysed practically pure toluene, the remainder of the incoming heptane being largely cracked to lower gaseous aliphatic hydrocarbons.

Effect of Temperature.—To trace the effect of temperature, conversions at higher rates of heptane flow may be cited. Fig. 4 shows yields on chromium oxide gel at temperatures from 476° to 516°C . with check runs at the lower temperature after the two runs at the two highest temperatures. That the process, even at the highest temperatures, was substantially a dehydrogenation-aromatisation is evident from the gas analyses on samples taken at various stages in the experiments. The rate of liquid flow was much faster in these experiments in order to reveal adequately the effect of temperature. In each case 0.30 c.c. of liquid heptane were passed per minute as vapour over 15 g. of the chromic oxide gel catalyst.

²³ *Brennstoff-Chem.*, 1939, 20, 1.

²⁴ Kohlschutter, *Z. anorg. Chem.*, 1934, 220, 370.

TABLE II.—GAS ANALYSIS FROM AROMATISATION OF *n*-HEPTANE AT 476–516° C. (NITROGEN-FREE BASIS).

Temp. °C. of Expt. = Nature of Sample.	476 Second 2 Litres.	486 Final 2 Litres.	496 Final 2 Litres.	506 Second 2 Litres.	516 Second 2 Litres.
CO ₂ per cent.	0·24	0·22	0·24	0·13	0·12
Unsat.	0·97	1·08	0·98	0·77	0·84
O ₂	0·59	0·43	0·70	0·38	0·24
H ₂	90·4	88·64	88·2	87·6	87·6
CO	0·71	1·74	1·58	1·29	0·73
Sat. H.C.	7·18	7·98	8·34	9·84	10·5

The data indicate an upward trend in the cracking reactions as shown by the increasing percentage of saturated hydrocarbons. Beyond 526° C. the tendency becomes much more pronounced, the percentages of saturated hydrocarbons at 536, 546, and 566° showing 13·3, 14·5, and 19·7 per cent. respectively.

Reference to the curves in Fig. 4 shows that the rate of gas evolution progressively decreases as the reaction proceeds. Typical data at 476° C. are shown in Table III for the rate in c.c./min. at various time intervals over a 2½ hour run with 0·3 c.c. liquid heptane per minute over 15 g. of catalyst.

TABLE III.—RATE OF GAS EVOLUTION AT 476° AT VARIOUS TIME INTERVALS.

Time interval	25	40	60	80	100	120	140
Rate, c.c. gas/min.	73	73	60	50	39	37	34

Since 0·3 c.c. liquid heptane, passing per minute, is equal to 0·22 g. or $0·22 \times 10^{-2}$ mol., the heptane vapour passing per minute is approximately 45 c.c. measured at normal temperature and pressure. The initial hydrogen yield is therefore about 1·5 mol. H₂/mol. heptane under the flow conditions obtaining at 476°. At 516° C. the hydrogen yield initially approximates 2 mols. per mol. heptane, corresponding roughly to 50 per cent. aromatisation per passage. After two hours of heptane flow the hydrogen yield falls at 476° to approximately 0·5 mol. per mol. heptane.

Regeneration of Catalyst Activity.—The decrease in activity of the catalyst with time has been shown to be due to poisoning by products other than those of the main reaction. Toluene added to initial heptane does not materially affect the initial rate. The activity of a spent catalyst can be restored by treatment with oxygen containing gases at the reaction temperature. Nitrogen with oxygen concentrations from traces to that found in air have all been employed successfully to restore catalyst activity, the time required for regeneration decreasing with increasing oxygen concentration and with increasing temperature. With gel type catalysts care must be exercised not to overheat the catalyst mass in the revivification process as sintering of the catalyst enormously decreases the aromatisation efficiency of the mass. During revivification, CO₂ and H₂O are copiously evolved from the catalyst indicating oxidation of the adsorbed products which poison the catalyst. The regeneration process properly conducted has no deteriorating effect on catalyst activity. Experiments on a given sample over a 30-day period, with daily regeneration, showed no perceptible change in catalyst activity, during which time more than 1·5 l. of heptane liquid had been passed over a 15 g. sample of chromic oxide gel.

Catalyst Poisons.—Water vapour which is strongly adsorbed by chromium oxide gel is a marked poison for the reaction. Three per cent. of water introduced with a standard heptane feed of 0.3 c.c./15 g. catalyst decreases the rate of gas evolution to one-fifth of the normal rate. The effect is reversible, however, and on elimination of water vapour from the inlet stream, a progressive restoration of catalyst activity occurs as H_2O is desorbed from the catalyst. Smaller concentrations of H_2O had proportionately less effect. At 475° C. under standard conditions the gas yield in the first hour in a series of experiments fell from 4.7 l. to 4.0 and to 3.4 l. respectively when 0.5 and 1 per cent. water vapour were introduced with the heptane. The solubility of water in heptane is so small, however, that no measurable difference in rate of dehydrogenation could be observed with heptane dried over phosphorus pentoxide and heptane which had stood in contact with water.

Oxygen and other water-yielding gases are similarly detrimental. At 450° the gas yield in the first hour decreased from 2.92 l. to 2.88 and 2.15 l. with oxygen concentrations equivalent to 0.1 and 0.5 per cent. respectively of the heptane flow.

Pretreatment of active gel catalysts with ethylene gas practically destroyed the catalyst activity. The surface could not be regenerated either by hydrogen flush or pure nitrogen flush, but responded to oxidation regeneration. Simultaneous pretreatment with ethylene and hydrogen did not affect the catalyst adversely. It is evident that the catalyst polymerises ethylene and adsorbs tenaciously the polymerised product giving temporary poisoning. With hydrogen present, ethane is formed and the polymerisation suppressed.

Nature of Liquid Products.—As typical of an average product obtained on a standard gel catalyst at 475° C. we cite the following data from an analysis of the yield from a 40 c.c. charge of liquid heptane in 120 minutes. The condensate showed the following characteristics: Sp. Gr. (20°/4°) 0.717; olefines, 15 per cent.; aromatics, 15 per cent. At the same time, a yield of about 6 l. of gas, 89 per cent. H_2 would be obtained.

With specially prepared chromic oxide gels these yields could be markedly exceeded. The following data illustrate this and show the variation in yield secured in successive half-hour intervals of collection of liquid product.

TABLE IV.—YIELDS OF LIQUID PRODUCTS FROM HEPTANE ON 15 G. ACTIVE CHROMIC OXIDE GEL.

Temp. °C.	Gas Evolution, Litres/hr.	Liquid Cut.*	Liquid Analysis.		
			Sp. Gr. 20°/4°.	Olefine.	Aromatics.
450	3	1	0.714	13.3	23.1
475	6	1	0.743	13.4	41.5
—	3.5	2	0.713	13.6	24.3

* The cut represents that obtained in the half-hour indicated by the number in this column, charging rate 0.3 c.c. liquid heptane per minute.

It will be noted from these data that the decreased gas yield with time is reflected in a larger decrease in the yield of aromatics. The deterioration of the catalyst influences aromatisation quite pronouncedly but the formation of olefines is little affected.

Olefines as Aromatic Source Materials.—On chromic oxide gel a wide variety of olefines have been converted to aromatic hydrocarbons

with simultaneous liberation of hydrogen. Typical data are cited in Table V.

TABLE V.—CONVERSION OF OLEFINES TO AROMATIC HYDROCARBONS
0.3 C.C. LIQUID PER MIN. PER 15 G. Cr_2O_3 GEL.

Olefines.	Temp. °C.	Mols. Gas : Mols. Olefine.	Liquid Products.				Gas Composition.			Time in Mins. for 50 Per Cent. Deteriora- tion.
			Sp. Gr.	Per Cent. Ar.	Per Cent. Sat.	Per Cent. Unsat.	H ₂ .	Sat.	Unsat.	
2 Me.-	424	0.8	0.720	20	20	60	93	6	1	10
pentene-2	474	1.0	0.755	32	7	70	56	34	10	30
3 Me.-	424	0.6	0.780	21	18	61	95	4	1	10
pentene-2	474	1.0	0.760	32	5	72	55	38	7	30
2 Et.-	424	0.6	0.720	20	20	60	93	6	1	10
butene-1	474	1.0	0.759	32	6	62	57	35	8	30
Heptene-1.	424	1.0	0.775	45	13	42	93	7	0	10
	474	2.2	0.840	90	2	8	89.5	4	6	40
Heptene-3.	420	1.5	0.78	48	12	40	—	—	—	10
5 Me.-	424	2.0	0.78	50	12	38	31	57	12	10
hexene-2	—	—	—	—	—	—	—	—	—	—
Octene-1	474	2.57	0.849	84	1	15	94	3	3	—

The experiments show that the rate of conversion to aromatics is initially more rapid than the conversion of saturated hydrocarbons but the deterioration in activity is also more rapid, undoubtedly due to more side-reactions depositing carbonaceous residues on the surface. The data reveal that cracking of the hydrocarbons is more pronounced with the olefines than with the saturated hydrocarbons under the same conditions.

Of special interest is the cyclisation of ethyl butene and of the methyl pentenes, since this is indicative of isomerisation to a configuration favourable to aromatisation as a step in the conversion process. It is in the case of these hydrocarbons that the cracking is most pronounced as can be seen by comparison of these with heptene-1 at 474°. This aromatisation of olefines is of interest also in relation to the early patent of Wietzel and Pfaundler who operated with oxide catalysts on liquid products from the high pressure polymerisation of gaseous olefines. These products would normally be aliphatic olefines either normal or branched chains. The results cited above show the feasibility of converting such into aromatic products.

We have summarised in the preceding pages a very considerable amount of research work which succeeded our initial investigations in this field. The detailed statements of results will be presented elsewhere. Here we wish to express our acknowledgments for the preliminary use of data accumulated by Drs. D. J. Salley, H. Fehrer, E. C. Kirkpatrick, and Messrs. S. Goldwasser and R. A. Briggs whose contributions are not specifically mentioned by literature references in the text.

Summary.

1. The problem of ring closure of open-chain hydrocarbons with formation of aromatics has been discussed from the historical aspect and examined from the standpoint of the available thermodynamic data.

2. The catalytic problem involved has been reviewed from the standpoint of fundamental catalytic properties and available indications from the literature.

3. With chromium oxide gel as a typical catalyst and normal heptane as typical paraffin hydrocarbon it has been shown that quantitative conversion to aromatic hydrocarbon can be secured.

4. The effects of contact time, poisons and temperature on the nature of gaseous and liquid products in the case of chromic oxide gel catalyst are cited as typical of a large group of oxide catalysts studied.

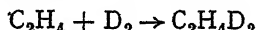
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THE MECHANISM OF CATALYTIC EXCHANGE REACTIONS BETWEEN DEUTERIUM AND OLEFINS.

BY GEORGE H. TWIGG.

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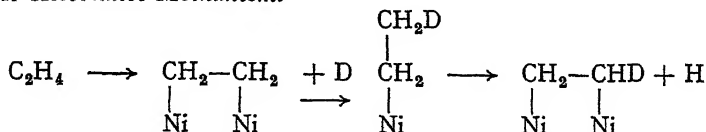
In one of the earliest papers on the chemistry of deuterium, Farkas, Farkas and Rideal¹ reported that when ethylene and deuterium interact on a nickel catalyst, in addition to the normal hydrogenation



an exchange takes place between the deuterium and the hydrogen in the ethylene $\text{C}_2\text{H}_4 + \text{D}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{D} + \text{HD}$. Two mechanisms for this exchange reaction are possible, one involving primary addition of a deuterium atom to the ethylene and the other primary loss of a hydrogen atom from the ethylene. It is the purpose of this paper to show how it has been possible to distinguish between these two mechanisms.

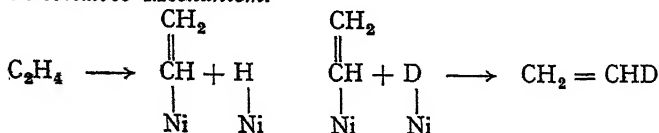
The two mechanisms may be represented diagrammatically as follows :

1. Associative Mechanism.



In this mechanism, which was first proposed by Horiuti and Polanyi,² the ethylene is adsorbed to the nickel catalyst through the opening of the double bond; a deuterium atom then adds to give a nickel ethyl radical which breaks up to reform an adsorbed ethylene molecule and liberate a hydrogen atom.

2. Dissociative Mechanism.



¹ Farkas, Farkas and Rideal, *Proc. Roy. Soc., A*, 1934, 146, 630.

² Horiuti and Polanyi, *Trans. Faraday Soc.*, 1934, 30, 1164.

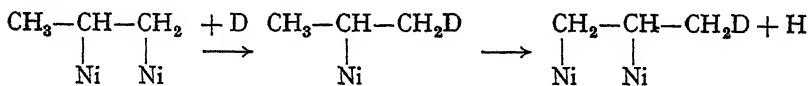
This mechanism, proposed by Farkas and Farkas,³ involves the adsorption of the ethylene through a breaking of a C—H bond and the loss of a hydrogen atom; exchange then occurs through the addition of a deuterium atom to the $-C_2H_3$ fragment.

The existing evidence tends against the dissociative theory. The low temperatures at which exchange between ethylene and deuterium occurs are in contrast to the high temperatures required for ethane which is known to proceed through a dissociative mechanism. Exchange between ethane and deuterium only takes place slowly at $100^\circ C.$,⁴ whereas that between ethylene and deuterium has been detected at as low as $-80^\circ C.$ ⁵

In order to gain more information as to the mechanism of the exchange reaction, experiments were made on the kinetics using ethylene and deuterium and comparing the exchange reaction with the hydrogenation which proceeded simultaneously. These experiments have been described elsewhere.⁶ The results of this work showed that it was not possible definitely to distinguish between the two mechanisms purely from a study of the kinetics. The rate of reaction for both exchange and hydrogenation was, at $156^\circ C.$, independent of the ethylene pressure, and proportional to the first power of the deuterium pressure; and the rate controlling step in exchange was not the actual exchange process but one involving molecules of deuterium.

It was, however, possible to distinguish between the two mechanisms by a direct experiment. If the dissociative mechanism is the one operative in exchange, then when light ethylene C_2H_4 and heavy ethylene C_2D_4 are allowed to interact on an active catalyst, exchange between these two ethylenes should take place giving rise to compounds of the type $C_2H_2D_2$, etc. Whereas, if the associative mechanism is the true one, then since the hydrogen (deuterium) necessary for the intermediate complex is absent, no exchange at all should occur. Experiments⁷ showed that there was no detectable exchange between light and heavy ethylene under conditions where exchange between ethylene and deuterium was quite rapid. The exchange reaction, therefore, proceeds through the associative mechanism.

Further confirmation of the associative mechanism can be obtained from a study of the exchange reactions of higher olefins. It is a necessary corollary of this mechanism that all the hydrogen atoms in the olefine and not just those attached to the double bond, should be equally exchangeable with deuterium. The case of propylene may be represented diagrammatically as follows:



In the intermediate stage, the two methyl groups attached to the central carbon atom are identical, and either may dissociate to reform the adsorbed propylene molecule. In this way, a propylene molecule can be produced in which a deuterium atom has been introduced into the methyl group. If the dissociative mechanism for exchange were correct, the

³ Farkas and Farkas, *J. Amer. Chem. Soc.*, 1938, **60**, 22.

⁴ Morikawa, Benedict and Taylor, *ibid.*, 1936, **58**, 1445, 1795.

⁵ Morikawa, Trenner and Taylor, *ibid.*, 1937, **59**, 1103.

⁶ Twigg and Rideal, *Proc. Roy. Soc., A*, 1939, **171**, 55.

⁷ Conn and Twigg, *ibid.*, 70.

hydrogen atoms in the methyl groups should be as unreactive as in ethane. The presence or absence of total exchange in the higher olefines thus provides a conclusive test of the mechanism.

Experiments have been carried out to determine the extent of exchange using a number of methyl substituted ethylenes. The apparatus and technique used in these exchange experiments have been described previously.⁶ The reaction vessel containing the catalyst was heated in a furnace to 97° C.; equal quantities of the olefine and deuterium were allowed to react and the deuterium content of the hydrogen ($u_{eq.}$) at the equilibrium point of the exchange reaction was determined as previously described. The results obtained are shown in Table I.

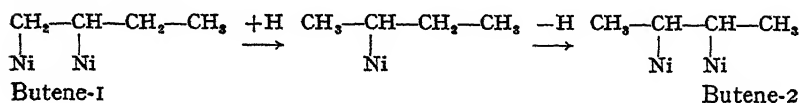
The second column A gives the classical values of $u_{eq.}$ calculated on the assumption that only the hydrogen atoms attached to the double bond can exchange (dissociation hypothesis). The third column B gives the classical values of $u_{eq.}$ on the basis of all the hydrogen atoms in the olefine exchanging (association hypothesis). The observed values of $u_{eq.}$ show

TABLE I.

Compound.	Classical $u_{eq.}$ per cent. A.	Classical $u_{eq.}$ per cent. B.	Observed $u_{eq.}$ per cent
Ethylene . . .	33.3	33.3	32.4
Propylene . . .	40	25	25
Butene-2 . . .	50	20	18
Isobutene . . .	50	20	13
Trimethylethylene .	66.7	16.7	14

very definitely that all the hydrogen atoms in the olefine are exchangeable. Experiments carried out under identical conditions with ethane showed no trace of exchange. In addition, graphs showing the course of these exchange reactions with time were smooth curves without any breaks, thus showing that all the hydrogen atoms in the molecule were equivalent with regard to exchange. These facts prove conclusively that exchange between olefines and deuterium on a nickel catalyst takes place through the associative mechanism.

A further consequence of the associative mechanism is seen from the diagram above. In the case of the propylene molecule shown there, the double bond has moved from the 2 : 3 position to the 1 : 2 position during exchange. This can be shown more clearly in the case of the normal butenes:

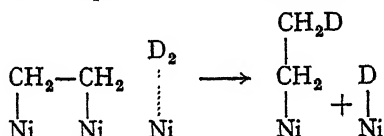


Double bond migration can thus take place through an exchange process; this reaction, however, will not occur in the absence of hydrogen.

The occurrence of double bond migration has been confirmed. The transformation butene-1 \rightarrow butene-2 was chosen to test this *a*, because the equilibrium point lies almost wholly on the butene-2 side, and *b*, because analysis could be readily effected by measuring the vapour pressure of the butene at -78° C. after removal of the hydrogen. In one experiment, equal quantities of butene-1 and hydrogen were allowed to interact at 133° C. on a catalyst active for exchange. The vapour

pressure of the butene-1 at -78°C . before the experiment was 10.6 mm., while the vapour pressure of butene-2 was 7.8 mm. The vapour pressure of the butene obtained after allowing the reaction to proceed for nineteen minutes was 8.8 mm. During this period, 10 per cent. of the butene was hydrogenated to *n*-butane. Since the vapour pressure of butane is greater than that of either butene, the presence of butane in the butene does not invalidate the qualitative nature of the analysis, which shows that double bond migration has taken place. No transformation of butene-1 to butene-2 occurred in the absence of hydrogen. These facts again confirm the validity of the associative mechanism for exchange. Further work of a quantitative nature is being carried out on this problem of double bond migration.

The experiments above give information as to the adsorption of the olefine and the mechanism of the actual exchange process. They do not, however, give any information about the adsorption of the deuterium or the rate-determining step in the reaction. In the previous paper⁶ it was shown that the catalyst surface was completely covered with ethylene to the exclusion of the deuterium and that the rate of exchange was controlled by the adsorption of the deuterium through such a step as



To gain more information about the rate-determining step, the energies of activation for exchange and hydrogenation for ethylene, propylene, butene-2 and isobutene were measured. The temperature range covered

55–120° C. was below the point at which the apparent energy of activation becomes temperature dependent. The experimental details have been described previously.⁶ In these experiments, the reaction vessel was heated in a furnace. Equal quantities of the olefine and deuterium were used, and the initial rates of exchange $-\left(\frac{du}{dt}\right)_0$ and

of hydrogenation $-\left(\frac{dp}{dt}\right)_0$ were determined. The activity of the catalyst was measured at the beginning and end of each day's working, and values for the exchange experiments interpolated. The results obtained are shown in Figs. 1, 2, and 3.

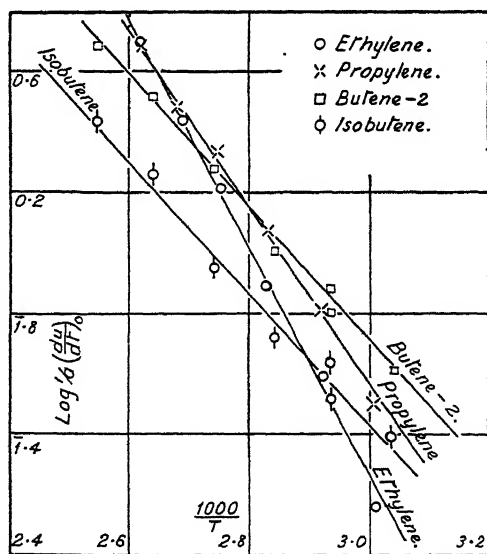


FIG. 1.—Temperature dependence of the exchange reaction.

The ratio rate of exchange/rate of hydrogenation (E/H) is given by $E/H = p_{D_2} \left(\frac{du}{dt} \right)_0 / \left(\frac{dp}{dt} \right)_0$. The values of the energies of activation obtained in k.cal. are given in Table II.

TABLE II.

Compound.	Exchange E_X (Fig. 1).	Hydrogenation E_H (Fig. 2).	$E_X - E_H$ (Fig. 3).
Ethylene . .	17.2 ± 0.5	8.2 ± 0.5	9.0 ± 0.2
Propylene . .	13.7	6.0	8.0
Butene-2 . .	10.0	3.3	7.0
Isobutene . .	10.0	3.3	7.0

The wide differences found in the energies of activation, combined with the similarity in the absolute rates of reaction are somewhat surprising.

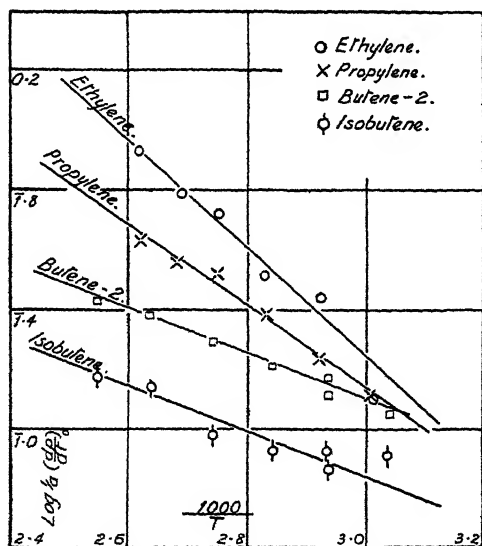


FIG. 2.—Temperature dependence of the hydrogenation reaction.

It is possible that the differences in these energies of activation are due to the fact that these measured energies contain some factor involving the adsorptions of the reactants on the catalyst. In the temperature range covered, the kinetics indicate that the rate of reaction is independent of the ethylene pressure and proportional to a power of the deuterium pressure slightly less than unity. Classical kinetics indicate that the measured energy of activation should be equal to the true energy less the heat of adsorption of the deuterium. It has been shown that the deuterium is not chemisorbed but is held in the van der Waals' layer above the chemisorbed ethylene. Consequently, the heats of adsorption involved are the heats of van der Waals' adsorption, which are not large enough to account for the observed differences in energy of activation between ethylene and the other olefines. It has been shown by Kistiakowsky and co-workers⁸ that the heats of hydrogenation of the olefines decrease with increasing molecular weight. This would suggest that when the olefine is adsorbed to the surface with opening of the double bond, the heat of adsorption and consequently the strength of the nickel-carbon bond should decrease with increasing molecular weight of the olefine. This

⁸ Kistiakowsky, Ruhoff, Smith and Vaughan, *J. Amer. Chem. Soc.*, 1935, **57**, 876.

would produce a decrease in the energy of activation on going from ethylene to the butenes. The decrease to be expected from the figures of Kistiakowsky,⁸ however, is insufficient to account for that found in these experiments. Another possibility is that the differences may be due to the closeness of packing of the olefine on the surface. The larger the olefine molecules, the larger the gaps between them in the saturated layer on the surface; the penetration of the deuterium into the olefine layer and the interaction with the nickel-carbon bond will thereby be facilitated and the energy of activation for the higher olefines reduced. It is probable that all these factors are operative, though it is impossible to say which is predominant.

The values of E/H graphed in Fig. 3 are the ratios of the number of molecules of deuterium undergoing exchange to the number undergoing hydrogenation. It will be seen from Fig. 3 that the values of E/H increase from ethylene to butene. This is to be expected from the increase in the ratio of exchangeable hydrogen to double bonds. The ratios of E/H for the three olefines are somewhat larger than would be expected on this basis, being approximately Et:Pr:Bu = 1:2:3 at 90° C., whereas from the ratios of exchangeable hydrogen one would expect Et:Pr:Bu = 1:1.5:2.

It has been seen from Figs. 1 and 2 that the correlation between energy of activation and absolute rate of reaction expected on the classical theory of heterogeneous catalysis is not fulfilled. It would be expected that, in the exchange reaction for example, with the differences in energy of activation found here, the rate of reaction for propylene would be about 10^2 times and for the butenes about 10^4 times that for ethylene; whereas they are approximately the same in the temperature region studied. A similar discrepancy exists for the hydrogenations. It will be seen, however, from Fig. 3, that for the exchange/hydrogenation ratios, this discrepancy is almost absent and the absolute values of these ratios for the four compounds are in the order which would be expected from the energy values $E_X - E_H$ associated with them. In particular, it will be noticed that the ratios for butene-2 and isobutene are coincident as would be expected from the fact that they have identical $E_X - E_H$ values. It would thus seem that in taking the exchange/hydrogenation ratios we have eliminated the factor which disturbs the correlation between energy of activation and absolute rate of reaction. These facts would also support the view that all these reactions take place on one uniform type of catalytically active centre.

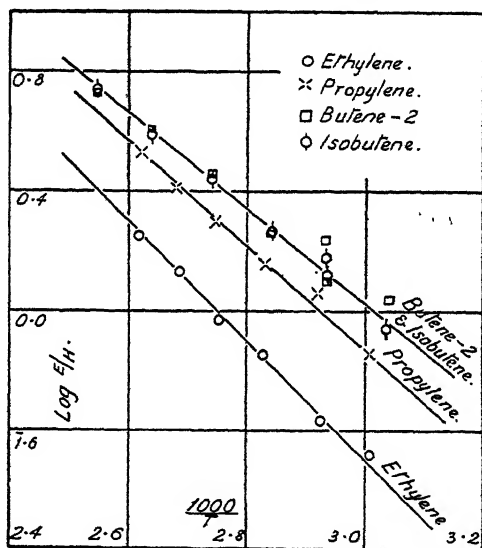


FIG. 3.—Temperature dependence of the exchange/hydrogenation ratio.

Summary.

The mechanism of the exchange reaction between deuterium and olefins on a nickel catalyst is discussed. It is shown that exchange takes place through an associative mechanism; the olefine molecule is adsorbed to the catalyst at two points through the opening of the double bond; a deuterium atom adds to form a nickel-alkyl radical which then decomposes to reform the adsorbed olefine molecule and release a hydrogen atom. Confirmation of the mechanism is obtained from the fact that all the hydrogen atoms in the higher olefins are exchangeable with deuterium under conditions where no exchange takes place between ethane and deuterium. A prediction on the basis of the associative mechanism that double bond migration should accompany exchange has been verified; no double bond migration occurs in the absence of hydrogen.

Energies of activation for exchange and hydrogenation have been determined over the temperature range 55-120° C. using ethylene, propylene, butene-2 and isobutene. These values decrease considerably with increasing molecular weight of the olefine; possible reasons for this are discussed.

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Cambridge.*

GENERAL DISCUSSION.*

Dr. R. H. Griffith (*London*) said: The review by Farkas of examples of the isomerisation of hydrocarbons recalls some observations which were made during experiments on the catalytic dehydrogenation of dekaline. When this process was carried out in contact with Cr_2O_3 , TiO or metallic Cu deposited on MgO at 500°, an intense blue colour appeared in the reaction products. This was due to a hydrocarbon which retained its colour in the vapour phase and, although the complete separation of this substance from naphthalene was difficult, it was almost certainly azulene, $\text{C}_{10}\text{H}_{10}$, so that the ring system must have changed from that of the dekaline skeleton to one containing a five-carbon and a seven-carbon ring. This indicates a more profound alteration of the original hydrocarbon than that involved in the disproportionation of cyclo-olefines.

It is also significant that when a metallic oxide, such as chromic oxide, or molybdenum trioxide is reduced by hexane, benzene or cyclohexane, the bulk of the oxygen removed appears as carbon dioxide,¹ and there must accordingly be complete rupture of the C—C bonds at an early stage of the change. The difference between such cases and those where a catalytic reaction takes place on the solid is apparently one of degree rather than of kind.

Dr. W. Jost (*Leipzig*), said: Though an associative mechanism would explain the observed facts, it might equally be possible to reconcile the observation, with higher olefins, with a dissociative mechanism. On account of the resonance energy, C_3H_4 would split off a hydrogen atom preferentially to produce an allyl radical $\text{H}_2\text{C}=\dot{\text{C}}\text{H}-\text{CH}_2$, to which a

* On the four preceding papers.

¹ Griffith, Hill and Plant, *Trans. Faraday Soc.*, 1937, **33**, 1419.

D atom could be added to give a C_3H_6 with exchange in the CH_3 group. In accordance with this butene might split to give a methyl-allyl radical $H_2\overset{1}{C}-CH-\overset{2}{CH}-CH_3$, in which the bonds 1 and 2 are equivalent; a deuterium atom then could be added to give either 1 or 2 butene in accordance with experiments.

Dr. J. K. Roberts (*Cambridge*) said: Farkas has, I think rightly, pointed out the importance of a knowledge of the elementary processes in catalytic reactions. The first of these that he discusses is the interaction of H_2 itself with a metal catalyst.

To explain their results on the *ortho-para* conversion on metals, Bonhoeffer and he proposed a mechanism involving the adsorption with dissociation of *para*-molecules and subsequent recombination and evaporation from the adsorbed film in equilibrium proportions. Dr. Farkas assumes throughout his contribution that this mechanism is correct and states it clearly in the first paragraph of his summary where he says: "The rate of dissociation can be measured by the *ortho-para* conversion of hydrogen or deuterium or by the reaction $H_2 + D_2 \rightleftharpoons 2HD$."

I think it is important to point out that, in one case at least, this assumption is not in accord with other experimental facts. One of the metals on which the *ortho-para* conversion was studied by Bonhoeffer and Farkas was W, and the results obtained with this metal did not differ in any important respect from those obtained with other metals. There was a comparatively rapid conversion at room temperature.

I have studied the adsorption of H_2 on W by different methods, one of them the most direct possible, and have shown² that at room temperature a bare W surface exposed to H_2 is immediately covered with a complete layer of the gas, the number of H atoms in the adsorbed film being equal within the experimental error to the number of W atoms in the surface. This film is absolutely stable at room temperature, *i.e.*, it does not evaporate appreciably into the best possible vacuum. Now the mechanism proposed by Bonhoeffer and Farkas requires a rapid evaporation of recombined molecules from the adsorbed film to account for their experimental results, and a continuous replenishment from the gas phase. It is thus excluded.

It therefore appears likely that, in the case of W, the *ortho-para* conversion takes place through the interaction of molecules in a second layer with those adsorbed directly on the W. The details are at present a matter of speculation, but one point may be mentioned. I have shown³ that any immobile film, in which each molecule from the gas phase which condenses does not occupy one site and one site only and in which the probability of condensation does not depend on the state of occupation of neighbouring sites, will not cover the metal surface completely, but will in its final state have holes or gaps in it. By an immobile film is meant one in which each adsorbed particle remains on the site on which it is first adsorbed. These holes or gaps may well be important centres of catalytic activity and it may be molecules adsorbed over them which undergo the *ortho-para* conversion. These considerations should be taken into account in discussing the details of the mechanism of catalytic hydrogenation processes.

Reference should also be made to the experiments of Burdon⁴ on Hg. Some experiments of Oatley⁵ on Pt are suggestive, but, owing to effects due to diffusion, not conclusive in the present connection.

Dr. A. Farkas (*Jerusalem*) (*communicated*): The evidence brought forward by Twigg against the dissociative mechanism and in support of

² J. K. Roberts, *Proc. Roy. Soc., A*, 1935, **152**, 452.

³ J. K. Roberts, *Nature*, 1935, **135**, 1037; *Proc. Roy. Soc., A*, 1935, **152**, 471; *Proc. Camb. Phil. Soc.*, 1938, **34**, 586.

⁴ R. S. Burdon, *Proc. Physic. Soc.*, 1935, **47**, 460.

⁵ C. W. Oatley, *ibid.*, 1939, **51**, 318.

the associative mechanism is not quite convincing. The different rates of exchange for C_2H_6 and C_2H_4 cannot be regarded as necessarily indicating that different mechanisms are involved in the exchange reactions of C_2H_6 and C_2H_4 . In fact, one would not expect similar rates of exchange in view of the different adsorbabilities of C_2H_6 and C_2H_4 . The absence of an interaction between C_2H_4 and C_2D_4 can be due to the circumstance referred to in my paper.⁶ The fact that all hydrogen atoms of higher olefines are exchangeable is not in contradiction to the dissociative theory, as all hydrogen atoms of saturated hydrocarbons are exchangeable and this latter type of exchange is certainly most easily explained by the dissociative theory. The catalytic migration of double bonds has already been observed in the absence of hydrogen,⁶ and the addition of hydrogen should accelerate this type of reaction even according to the dissociative mechanism for the same reason as referred to above.⁶ Still, I should not venture to propose that the correctness of the dissociative mechanism cannot be disputed. I would agree with Rideal that more experiments are needed before the final decision can be made. I should like to emphasise, however, that whatever the mechanism of the catalytic exchange reaction of unsaturated compounds, it is certainly different from and independent of the mechanism of the hydrogenation reaction.

Dr. G. H. Twigg (*Cambridge*) said: I am unable to criticise Jost's theory for double bond migration by dissociation from the point of view of resonance, but it seems that this mechanism, which is similar to one suggested by A. Farkas (eqn. 15, p. 914), must be ruled out by the principle of microscopic reversibility; for the H atom is removed in one way and restored in a different way, and to a part of the molecule not in contact with the catalyst. The reverse step in the equation involves the loss of a H atom from one part of the molecule simultaneously with attachment of a different part of the molecule to the catalyst, and thus is improbable.

In the paper of A. Farkas it is suggested that absence of exchange between light and heavy C_2H_4 does not disprove the dissociative mechanism for exchange, on the grounds that the recombination $D + C_2H_3 \rightarrow C_2H_3D$ may be slowed up by the D atom concentration being low. In the actual experiments made with C_2H_4 and C_2D_4 , however, this is not so, as the H(D) atom concentration is practically the same as in the exchange between C_2H_4 and D_2 . For in the latter reaction, since the slow step was found to be adsorption of the D_2 , the dissociation and recombination of the C_2H_4 would be fast and the stationary D atom concentration would be the dissociation concentration of C_2H_4 on the surface, *i.e.*, the same as in the exchange between the two ethylenes in the absence of H. Consequently, the recombination is equally fast in both reactions, and exchange between C_2H_4 and C_2D_4 would not be held up on this account.

In dealing with hydrogenation Farkas makes the assumption that part of the catalyst surface is bare, and that on this, dissociation and recombination of H_2 can proceed. Without going into the mechanism of the *para*-hydrogen conversion, I might say that in the experiments with C_2H_4 I found that the catalyst was completely covered with C_2H_4 below $160^\circ C$. and that there were no H atoms on the surface. There is no true *para*-hydrogen conversion in the presence of C_2H_4 at low temperatures. The apparent conversion found is due to the H_2 molecules partaking in exchange, as has been shown by examining the reaction $H_2 + D_2 \rightleftharpoons 2HD$ page 910 for the number of H_2 molecules recombined in presence of C_2H_4 , simultaneously with exchange.⁷ The figures which Farkas gives on must thus be regarded as being due, not to direct *para* conversion, but to exchange.

In section 3 (*d*) of Dr. Farkas's paper, it is said that no example of racemisation of optically active hydrocarbons has been observed. This

⁶ Page 906.

⁷ Twigg and Rideal, *Proc. Roy. Soc., A*, 1939, **171**, 55.

is only to be expected, as dissociation is essentially a high temperature process. This observation is thus an argument against dissociation being the mechanism of low temperature exchange reactions of olefines. The loss of optical activity of ricinoleic acid during catalytic hydrogenation is probably due to the fact that double bond migration by the associative mechanism takes place.

Finally, the proof of the fact that exchange in olefines goes by the associative mechanism is important, as it gives evidence as to the mode of

adsorption of olefines on the catalyst, *viz.*, $\begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{Ni} \quad \text{Ni} \end{array}$. Calculations which

I have made on the fitting of the olefines to the surface, assuming adsorption on the 111 plane, show that they fit very well, with only a slight change of the Ni—C—C angle from the tetrahedral angle. In the case of C_2H_4 , interaction between neighbouring adsorbed molecules is slight and consequently C_2H_4 can cover the whole surface, as has been shown experimentally. In the case of higher olefines, however, according to calculation, interaction becomes considerable and these olefines should be unable to cover the whole surface even at saturation. This has been shown experimentally, using the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$, to be the case for isobutene and trimethylethylene.

Dr. A. Farkas (Jerusalem) (communicated): In reply to Dr. Roberts, Professor Bonhoeffer and I have pointed out in one of our earliest papers on the catalytic *ortho-para*-conversion* that those areas of a catalyst which adsorb hydrogen very strongly will be *inactive* in the catalytic conversion. It is true that the proposed mechanism of the *ortho-para*-conversion requires a rapid and continuous re-evaporation of hydrogen from an adsorbed film on the catalyst but it does not require this rapid evaporation to occur from *all* or *most* of the catalytic surface. Thus Roberts' conclusion that the proposed mechanism cannot be maintained is not justified. This is the more so, since *ortho-para*-conversion was also found on Pd, Pt, Ni, and Fe, which are well known to take up and to give off hydrogen readily. Furthermore, it is not at all certain that Roberts' findings on W apply also to any other metal.

It is possible that although most of the surface of the W catalyst is covered with a strongly-held immobile layer of hydrogen atoms, certain areas do not hold the hydrogen so strongly, and are catalytically active. As indicated by Roberts, the "gaps" in the adsorption layer might be just these active areas. Thus I do not see any contradiction between Roberts' adsorption measurements and the proposed mechanism of the catalytic *ortho-para*-conversion which has proved very plausible in the course of the last eight years while dealing with the most various kinds of catalytic reactions of hydrogen.

I should be very interested to hear from Roberts what alternative mechanism he would suggest for the catalytic *ortho-para*-conversion, as I should not like to give up the old mechanism before a better one has been found. Surely any mechanism involving an interaction with the strongly-held immobile layer of hydrogen atoms must be ruled out on energetic grounds. If there is a second layer of hydrogen on top of the first, then the proposed mechanism might apply to this second layer. After all, from the point of view of catalysis it is irrelevant whether the bare metal or the metal covered by an immobile layer of hydrogen serves as catalyst.

I cannot agree with Twigg that the mechanism proposed for the migration of the double bond (equation 15, p. 914) is contrary to the principle of microscopic reversibility. I have not specified which part of the hydrocarbon molecule is in contact with the catalyst, and anyway there is no reliable method to decide this question.

I am afraid I am unable to follow Twigg's argument by which he tries to refute my assertion that even according to the dissociative mechanism

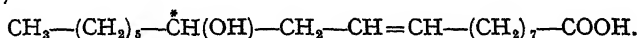
* *Z. physik. Chemie, B*, 1931, **12**, 243.

the concentration of the hydrogen atoms in the adsorption layer play a decisive part in determining the rate of the exchange reaction between hydrocarbons. Twigg admits that in the interaction between C_2H_4 and D_2 the adsorption of D_2 is the slow step. Then obviously the exchange reaction must come to a standstill if the rate of adsorption of D_2 is zero, *i.e.* if no D_2 is present at all. The mistake in Twigg's argument has arisen through his overlooking the recombination of the hydrogen atoms, which are being formed by the dissociation of the hydrocarbon molecules, to hydrogen molecules.

The figure I give on page 910 as the number of hydrogen molecules recombined per second in the presence of C_2H_4 refers actually to direct *para*-conversion, and not to exchange, as Twigg suggests. This is quite obvious, since under the conditions of this experiment no exchange is found with heavy hydrogen.

In section 3(*d*) of my paper, I state that no example is yet known for the catalytic racemisation of optically active hydrocarbons. This is not an "observation" and no "argument" against anything as Twigg puts it, but is only the simple expression of the fact that this kind of process has not yet been investigated.

The optical activity of the ricinoleic acid has nothing to do with the double bond, but is due to the asymmetrical carbon atom (marked by an asterisk)



Therefore a migration of the double bond as suggested by Twigg (the mechanism of the migration is irrelevant) cannot account for the loss of optical activity. Any isomer of ricinoleic acid which can be formed by such a migration should be optically active. Furthermore, on hydrogenation only one kind of dihydro-ricinoleic acid could result whether a migration of the double bond has or has not taken place, and this substance also should be optically active.

Dr. J. K. Roberts (*Cambridge*) said: At the end of the last paragraph but one of section 1 of his paper Farkas states that "In the presence of another reaction partner the displacement of hydrogen will become manifest by a lowering of the rate of *para-ortho*-conversion or of the reaction $H_2 + D_2 \rightleftharpoons 2HD$. Thus by varying the concentration of the hydrogen and its reaction partner it is possible to deduce adsorption isotherms for both from the rate of the interchange (*i.e.*, *para-ortho*-conversion, etc.) reactions." From this statement I inferred that one must include as an essential part of his proposed mechanism the supposition that a large part of the surface is involved in the conversion, *i.e.*, that a rapid and continuous re-evaporation of hydrogen takes place from most of the surface, which, as the pressure variation of the rate indicates, must be regarded as only partially covered with adsorbed hydrogen. If this supposition is dropped, I agree with him that the mechanism of dissociation and recombination on the metal must be retained as a possibility, but without the supposition I doubt very much whether reliable adsorption isotherms can be obtained by the above method. My criticism was directed against the mechanism as a whole including this supposition.

I agree that, if there is a second layer of hydrogen, and, I would add, provided the hydrogen in this upper layer is dissociated, the mechanism proposed by Dr. Farkas including the above supposition might apply to this layer, but I think that, when one is trying to picture in detail the process of the catalysis of the conversion on tungsten, it may prove relevant to know the nature of the surface on which the catalysis is occurring, *i.e.*, to know whether it is a metal surface or a surface covered with hydrogen.

A reaction of a different type, that would not be excluded on energetic grounds, would I think be an exchange reaction between a molecule adsorbed in a second layer and an atom in the atomic layer. This leaves the atomic layer essentially unchanged.

Dr. G. H. Twigg, in reply (communicated): The mechanism of double bond migration suggested by Farkas (eqn. 15, p. 914) requires a cyclic process, which is only possible if the two methods of arriving at the intermediate (adsorbed) state are equally probable. These two methods are (1) the first step of equation 15, and (2) the reverse of the second step. The latter is much less probable than the former as it involves simultaneously attachment of a C atom to the catalyst, loss of a H atom from a different C atom, and the transfer of the double bond.

I think that Farkas is not quite right in saying that the exchange reaction must come to a standstill if the rate of adsorption of D_2 is zero. This is true certainly of the exchange between C_2H_4 and D_2 , but not necessarily of that between C_2H_4 and C_2D_4 . Since in experiments with D_2 present the adsorption of the D_2 is rate determining, the surface equilibrium $C_2H_4 + H \rightleftharpoons C_2H_4_{ads}$, on the dissociative theory is set up. The rate of exchange between C_2H_4 and C_2D_4 is then governed by the dissociation and recombination, *i.e.*, the rate of exchange $\propto [C_2H_4][H]$ which is $\propto [C_2H_4]_{ads}$. The absence of $p-H_2$ conversion shows that $[C_2H_4]_{ads} + [C_2H_2] \approx 1$. In my argument I assumed that $[C_2H_4]_{ads} \approx 1$ in absence of H_2 and therefore, not affected greatly by hydrogen pressure. This assumption can be tested by finding whether hydrogen appears in the gas phase when ethylene is adsorbed on the catalyst. If no hydrogen appears, then the surface is covered with undissociated C_2H_4 and the assumption is justified.

The difference between the results of Farkas and myself as regards direct $p-H_2$ conversion in presence of C_2H_4 may be due to the catalyst used. On nickel, I found no direct conversion at low temperatures; further, extrapolation of Fig. 3 (ethylene) of my paper gives a value for the exchange/hydrogenation ratio which agrees closely with the recombination/hydrogenation ratio of the figures given by Farkas.

I of course realised that the optical activity of ricinoleic acid is due to the asymmetrical C atom, and my suggestion was that migration of the double bond up to this C atom would cause it, through its attachment to the double bond, to lose its asymmetry.

Finally, I would like to make clear that, while disagreeing with Farkas as regards the mechanism of exchange with olefines, I agree with him that for saturated compounds exchange must go through dissociation.

PART III.—THE MECHANISM OF THE TECHNICAL SYNTHESIS AND TRANSFORMATION OF HYDROCARBONS.

SECTION A. REACTIONS OF THE FISCHER-TROPSCH PROCESS.

THE FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS, AND SOME RELATED REACTIONS.

By S. R. CRAXFORD.

Received 6th February, 1939.

In 1925 Fischer and Tropsch discovered that if carbon monoxide and hydrogen are passed over an iron or cobalt catalyst, suitably promoted and supported, at 200°-250° C., and at atmospheric pressure, long chain paraffin and olefine hydrocarbons are produced. Since then the synthesis has been studied intensively by Fischer and his co-workers, and also at the Fuel Research Station at Greenwich, and has proved to be a reaction of the most peculiar characteristics. The best catalysts now in use are of the type developed by Fischer and Koch,¹ containing for example, cobalt, thoria and kieselguhr in the proportions 100 : 18 : 100, and are prepared by precipitation as carbonates, followed by reduction with hydrogen at 375° C. The following remarks apply only to work with this type of catalyst.

1. If a freshly reduced catalyst is put in contact with a stream of synthesis gas, $\text{CO} + 2\text{H}_2$, at 190° C. and atmospheric pressure, carbon dioxide and methane are produced, and this reaction continues for several hours, after which the Fischer synthesis sets in and oil and water are formed instead of methane and carbon dioxide.² This initial formation of methane and carbon dioxide before the synthesis of oil starts, appears to occur with many different types of Fischer catalyst, even with iron ones,³ although some of the more active cobalt preparations behave, in addition, in a rather different way.⁴

2. The temperature range over which the synthesis of oil occurs is small. Even with a very active sample of catalyst the formation of oil is very slow below 175° C. and at the other end of the effective temperature range the formation of oil falls off sharply above about 225° C., but in this case the oil formation is replaced by a rapid formation of methane. These results are illustrated most clearly by the curves obtained by Tsuneoka and Murata.⁵

¹ F. Fischer and H. Koch, *Brennst. Ch.*, 1932, 13, 61.

² F. Fischer and K. Meyer, *ibid.*, 1931, 12, 225.

³ F. Fischer and H. Tropsch, *Ges. Abh. Kennntn. Kohle*, 1930, 10, 313.

⁴ E. F. G. Herington and L. A. Woodward (*next paper in this discussion*).

⁵ S. Tsuneoka and Y. Murata, *J.S.C.I. (Jap.) Suppl.*, 1937, 40, 478 B.

3. The methane synthesis persists actively at very much higher temperatures, for example 300°-350° C., and while this is occurring, the oxygen product is mainly carbon dioxide, and not water, as it is during the synthesis of oils.⁵

4. After a week or so of continued use for the synthesis of oil, the activity of the catalyst decreases but can be largely restored by passing hydrogen over it at the same temperature as is being used for the synthesis of oil. When this treatment is finished, and synthesis gas is again passed over the catalyst, there is a big contraction for the first few hours and carbon dioxide, and presumably methane are formed. Then after this, the synthesis of oil and formation of water, instead of carbon dioxide, set in.⁴

5. Finally, increasing the pressure to 50 or more atmospheres induces the formation of compounds containing oxygen, such as alcohols, acids and aldehydes, along with the hydrocarbon oils.⁶

These then are the more striking characteristics of the Fischer synthesis, and in an attempt to elucidate its mechanism, the following lines of approach have been investigated experimentally.

1. The Formation of Carbides.

It is significant that the only three metals which show any activity as Fischer catalysts at atmospheric pressure, namely, iron, nickel and cobalt, all react with carbon monoxide at 200° C. and higher to form carbides, and Fischer has always postulated that such carbides are formed as intermediate compounds in the synthesis of hydrocarbons. Bahr and Jessen⁷ found that freshly reduced cobalt reacts completely at 230° C. with carbon monoxide as :



At higher temperatures free carbon is formed as well. During the formation of the carbides the crystal lattice of the metal changes, nickel, for example, going over from a cubic to an hexagonal type of symmetry,⁸ which latter corresponds to the densest packing of the nickel spheres. The carbon atoms occupy spaces in this lattice and occur separated, and not in pairs together as they do in carbides derived from acetylene. Cobalt carbide begins to be unstable to heat above about 230° C. It reacts smoothly and rapidly with hydrogen at 250° C. going quantitatively to methane. The free carbon does not react with hydrogen below 330° C. And finally, in dilute acids, higher hydrocarbons are formed, cementite Fe_3C , for example, giving gaseous, liquid and solid hydrocarbons.

It is to be expected that the chemistry of the carbide of the cobalt in a Fischer catalyst might be rather different, as the cobalt may be in a much more reactive state than the cobalt used by Bahr and Jessen. For this reason experiments were carried out on the rate of formation and reduction of carbide on an active Fischer catalyst. The actual sample used, containing Co : ThO_2 : kieselguhr in the ratio 100 : 18 : 100, was prepared at the Fuel Research Station, by the standard method used there for the preparation of Fischer catalysts.⁹ The experimental results

⁶ F. Fischer and H. Küster, *Brennst. Ch.*, 1933, 14, 3.

⁷ H. A. Bahr and V. Jessen, *Ber.*, 1930, 63, 2227.

⁸ B. Jacobson and A. Westgren, *Z. physikal. Ch. B.*, 1933, 20, 361.

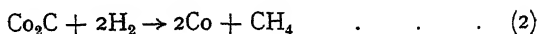
⁹ *Report of the Fuel Research Board*, 1938, 189.

are shown in Fig. 1 in so far as they are required for the following discussion, the curves being obtained by putting about 100 c.c. of gas in contact with 9 gms. catalyst and measuring the pressure change.

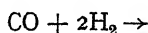
Curve 1 is for the reaction



Curve 2 is for



and curve 3 is for



In the first place, curve (1) shows that the catalyst forms carbide relatively rapidly at 200° C. by reaction (1), whereas ordinarily precipitated and

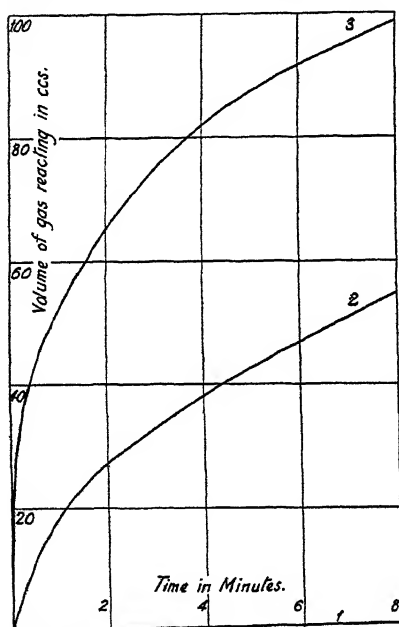
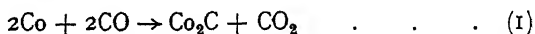


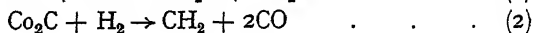
FIG. 1.—Rates of formation and reduction of carbide at 200° C.

reduced cobalt was proved to react only extremely slowly at 200° C., and even at 230° C. reacts very much slower than the Fischer catalyst at 200° C. The carbide formed by the Fischer catalyst reacts with hydrogen at 200° C. to give methane, according to curve (2), and as the curve shows, this reaction is very much faster than the rate of formation of the carbide. So much so, in fact, that the reduction of the carbide proceeds easily at 140° C., a temperature much lower than that required by Bahr and Jessen's sample. The hydrocarbon gas produced by the reduction of the catalyst carbide at this low temperature was found to have an "n" value (in $\text{C}_n\text{H}_{2n+2}$) of 1.12, showing that a small but definite amount of ethane, or higher hydrocarbon, was being formed at the same time as the methane.

Now during the Fischer synthesis, the catalyst is in contact with carbon monoxide and hydrogen simultaneously, so that if the synthesis involved the two alternating reactions

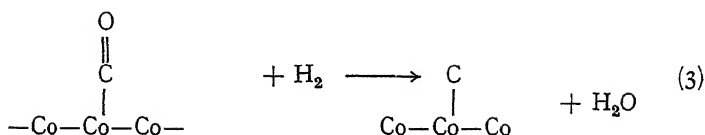


and



↓
→ higher hydrocarbons

carbide could never accumulate on the catalyst because the rate of reduction of carbide is so much greater than its rate of formation by reaction (1). But there is very good evidence that carbide does accumulate on the catalyst during the Fischer synthesis and hence that it is being formed by some reaction faster than (1), in fact, by the reaction



which is the only alternative to (1). The evidence that this reaction (3) does occur during the synthesis and that it is a faster reaction than (1) is as follows:

In the first place, the rate of the reaction of $\text{CO} + 2\text{H}_2$ with a Fischer catalyst has been measured under the same static conditions as were used for the determination of the rates of the other reactions. Granting that the reaction is proceeding by way of the carbide, the rate of formation of the carbide cannot be slower than the rate of the total reaction, and it may be a good deal faster. The rate of the total reaction is shown by curve (3) and this is much faster than either reaction (1) or (2).

Secondly, there is a proof on very general grounds that in the Fischer synthesis the first step is reaction (3) and not (1), because the oxygen product of the synthesis is water and not carbon dioxide. And it cannot be argued against this, that carbon dioxide, although first formed, might react with hydrogen to give water and carbon monoxide, because at 200°C . the water-gas shift equilibrium is entirely on the carbon dioxide side.

Finally, the evidence that carbide accumulates on the catalyst during synthesis, proves that it cannot be formed under these conditions by reaction (1). This evidence is undoubted, and depends on a number of different types of observations. During the course of the present experiments it was always found that if, after synthesis, the catalyst is pumped out and then treated with hydrogen at 200°C ., the hydrogen reacts rapidly to give methane. Similarly Fischer³ decomposed used catalysts with hydrochloric acid and obtained higher hydrocarbons as shown in Table I. A condensation analysis of the first gas is shown in

TABLE I.

Catalyst.	Weight Gms.	Volume of Gas. N.T.P. c.c.	Olefines. Volume Per Cent.	"n."	Paraffins. Volume Per Cent.	"n."
Fe—Cu	16.5	1630	6.9	—	6.5	—
Co—Cu	19.0	2300	6.4	3.03	1.0	3.00
Co—Cu	15.0	1570	1.0	—	0.3	—

TABLE II.

Per Cent.	Per Cent.	Per Cent.
CH_4 3.67	C_2H_4 1.83	H_2 85.1
C_2H_6 1.88	C_3H_6 1.55	N_2 1.78
C_2H_8 0.75	C_4H_8 1.2	—
C_4H_{10} 0.26	C_5H_{10} 1.38	—
Higher 0.72		

Table II. The only complete weight balance for a Fischer synthesis that has been published, is one obtained by Fischer and Tropsch³ for

an iron-copper catalyst (Table III), and shows clearly the formation of carbide in the initial period of the reaction. The figures are in c.c., reckoning the carbon as a gas.

TABLE III.—CARBON BALANCE.

Time, Hours.	As Hydrocarbons.			Carbide.	As Carbon Dioxide from		
	Detected.	Un-detected.	Wax.		Formation of Hydrocarbons.	Carbide.	Reduction of Catalyst.
0-2-25	66.0	—	—	79.4	66.0	79.4	39
2-25-8-25	607.6	21.7	8.4	36.1	628.4	36.1	158
8-25-14-25	562.7	127.8	8.4	—	661.3	—	—
14-25-20-25	516.4	151.4	8.4	—	644.5	—	—

The last piece of evidence for the formation of carbide during synthesis is of a very different nature, and is due to Göthel¹⁰ who measured the electrical conductivity of the powdered catalyst during synthesis and found that it varies in such a way as to show that carbide is being formed in increasing amounts as the synthesis proceeds.

From all these results it follows that the first stage in the Fischer synthesis is the reaction of chemisorbed carbon monoxide with hydrogen to give carbide and water. The next stage is the reduction of this carbide by hydrogen to give higher hydrocarbons. Although under some conditions this reduction is well known to give higher hydrocarbons, as for example, during the Fischer synthesis and when the carbides are dissolved in dilute acids, under other conditions methane alone is produced. The following section describes experiments, using the *ortho-para*-hydrogen conversion, to find out why the reaction sometimes takes one course and sometimes the other.

2. Experiments on the *Ortho-para* Hydrogen Conversion on the Catalyst during the Fischer Synthesis.

While the exact mechanism of the *ortho-para*-hydrogen conversion is still disputed, it is generally agreed that when the conversion is proceeding on a metal surface, hydrogen atoms must be present on that surface, and that the conversion will not occur in their absence. Thus the conversion may be used as a means of detecting the presence of hydrogen atoms on a metal surface, and the experiments to be described show how this method may be applied to the Fischer catalyst while the Fischer synthesis is occurring on it.

For if the gases used in the synthesis are $(\text{CO} + 2\text{H}_2^{\text{para}})$ or $(\text{CO} + 2\text{H}_2^{\text{equilibrium}})$, the reaction will proceed to the same extent as the two forms of hydrogen are identical chemically, and hence the effluent gases will be identical chemically in both cases. But by measuring the heat conductivity of the effluent gases in the two cases, the difference will give the proportion of hydrogen in the *para*-form in the first effluent gas, and hence the amount converted by its passage over the catalyst, during the progress of the reaction. The experimental arrangements are as shown in Fig. 2, and need no comment beyond the fact that the position of the tap X determines whether $(\text{CO} + 2\text{H}_2^{\text{para}})$ or $(\text{CO} + 2\text{H}_2^{\text{equilibrium}})$ is passed through the catalyst and then into the sampler and the conductivity gauge.

¹⁰ H. Göthel, *Grenzflächen-Katalyse*, M. Kröger-Hirzel, Leipzig, 1933, p. 67.

Such a conductivity gauge will measure very accurately the proportion of *para*-hydrogen in a sample of hydrogen free from other gases, but the presence of other gases such as carbon monoxide and methane makes the measurements difficult and the gauge readings are never very steady. It is estimated that on account of uncertainties of this nature the data in Table IV for the percentage conversion of *para*-hydrogen are only accurate to some 5 per cent., and in some individual cases may be just a little worse than this.

Unless otherwise stated the catalyst is always the cobalt-thoria-kieselguhr sample already described and supplied by the Fuel Research Station, Greenwich.

The results in Table IV may be summed up as follows: The experiments on an active Fischer catalyst show that while the Fischer synthesis is proceeding at about 200° C. to give hydrocarbon oils and very little methane, the *ortho-para*-conversion occurs only to a very small extent,

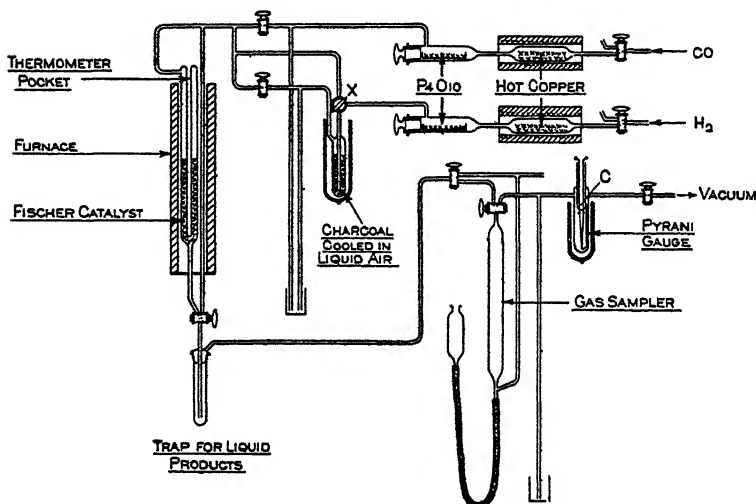


FIG 2 APPARATUS FOR THE FISCHER SYNTHESIS WITH ORTHO OR PARA HYDROGEN

but the conversion occurs freely for all the following conditions under which either there is no reaction, or else methane is being formed:

- (i) With normal synthesis gas, *i.e.*, $\text{CO} + 2\text{H}_2$, below 160° C. in which case there is no reaction.
- (ii) With synthesis gas at 200° C. for the first hour or so of the reaction, during which time methane, carbon dioxide and cobalt carbide are being formed, but no oil.
- (iii) With $\text{CO} + 24\text{H}_2$ at 200° C., even after 24 hours, with which gas mixture hardly any oil is formed, only methane.
- (iv) With synthesis gas above 250° C. Again methane is the product, and no oil.

The conclusion to be drawn from these results is that when Fischer oils are being formed there is very little conversion, and hence only very little atomic hydrogen on the catalyst surface. The reaction is therefore proceeding by way of molecular hydrogen. On the other hand in all cases where the product is methane, conversion does occur freely, and there is therefore atomic hydrogen present on the surface in sufficient amount to enter into the reaction, which it presumably does. These ideas are completely confirmed by the results for two abnormal catalysts given at the end of the table. One is an active Fischer catalyst poisoned by sulphur at 300° C. so that it is inactive for the Fischer synthesis at 200° C. but still

active for the synthesis of methane at 300° C. It catalyses the conversion actively at 300° C. while synthesising methane. The other is a cobalt catalyst obtained from another source, and which was treated with hydrogen

TABLE IV.

Catalyst.	Gas.	Temp. ° C.	Time from Start. Hours.	Gas Rate. litres/h.	Conversion of <i>Para</i> -Hy- drogen. Per Cent.	Reaction Products.
None	H ₂	200	—	—	0	
Active Catalyst	H ₂	200	—	—	100	
" "	CO+5.8 H ₂	200	0.5	5.0	> 95	CH ₄ , no oil.
" "	CO+5.8 H ₂	200	1.0	5.0	42	CH ₄ and oil.
" "	CO+5.8 H ₂	200	4.5	5.0	< 5	Oil, very little CH ₄ .
" "	CO+14 H ₂	200	0.25	5.0	> 95	CH ₄ only.
" "	CO+14 H ₂	200	1.0	5.0	66	CH ₄ and a little oil.
" "	CO+24 H ₂	200	0.25	3.6	> 95	CH ₄ only.
" "	CO+24 H ₂	200	3.0	3.6	60	CH ₄ and a little oil.
" "	CO+H ₂	128	5.0	2.9	> 95	No reaction.
" "	CO+5 H ₂	125	5.0	6.0	> 95	No reaction.
" "	CO+5 H ₂	145	5.0	6.0	> 95	No reaction.
" "	CO+2.75 H ₂	145	5.0	3.8	> 95	No reaction.
" "	CO+2.75 H ₂	160	3.0	3.8	75	CH ₄ and a little oil.
" "	CO+1.5 H ₂	175	6.0	2.6	75	CH ₄ and a little oil.
" "	CO+2 H ₂	175	24.0	3.1	75	CH ₄ and a little oil.
" "	CO+2 H ₂	200	4.0	10.0	70	Oil. For this experiment a very short catalyst bed and a high rate of flow was used.
" "	CO+2 H ₂	200	4.0	4.0	40	Oil. A very long catalyst bed was used, and the result shows that the latter part of the bed, which is not actively engaged in the synthesis, is not freely active for the <i>o-p</i> conversion.
" "	CO+2 H ₂	250	4.0	4.0	78	Very little oil, much methane and gasol. Molecular ratio of H ₂ O/CO ₂ is 8.25. If the water-gas shift and the <i>o-p</i> conversion inhibitions were running strictly parallel, the H ₂ O/CO ₂ ratio would have been 22: 78, i.e., 0.3.
" "	CO+2.4 H ₂	300	4.0	5.3	90	CH ₄ , a little gasol, no oil.
Active Catalyst carbided for 18 hours at 200°	H ₂	25	4.0	4.0	< 5	
	H ₂	200	0.3	4.0	92	The carbide is rapidly reduced at 200° C.
Active catalyst poisoned by sulphur at 300° C. so as to be entirely inactive for the Fischer synthesis at 200° C.	H ₂	18	4.0	4.0	0	
	CO+4 H ₂	200	4.0	4.0	86	No reaction.
	CO+4 H ₂	320	4.0	4.0	79	Rapid reaction to give CH ₄ .
Blue cobalt catalyst from another source	H ₂	200	4.0	4.0	> 95	No reaction.
	CO+2 H ₂	210	4.0	4.0	> 95	No reaction.
	CO+2 H ₂	286	4.0	4.0	5	Oil, gasol and methane.

at 375° C. in the normal way to reduce it. After this treatment a blue mass was formed which still contains oxygen and which gives no Fischer synthesis at 200° C. But at 286° C. it does synthesise a little oil, much gasol and some methane and under these conditions it gives very little conversion of *para*-hydrogen.

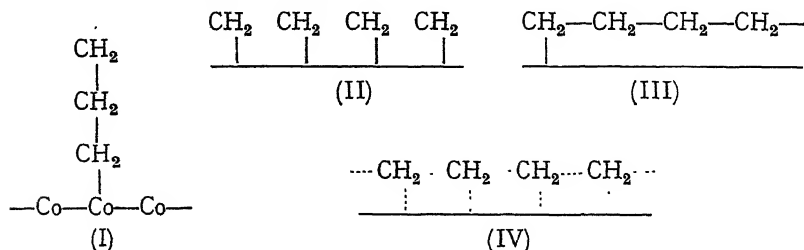
During the initial period of a normal Fischer reaction, when methane and carbon dioxide are being produced, and before the synthesis of oil sets in, it has already been shown that carbide is being built up on the catalyst, and another experiment has shown that a carbided catalyst does not catalyse the *ortho-para*-hydrogen conversion. Thus the inhibition of the conversion during the Fischer synthesis may most probably be due to the conditions being such as to maintain a big surface concentration of carbide. The inhibition of the conversion by the presence of carbide may also be accompanied by inhibition due to the adsorption of hydrocarbon products of the synthesis, because it is well known that whereas paraffin hydrocarbons such as ethane do not inhibit the *ortho-para*-hydrogen conversion on nickel at low temperatures, quite small amounts of ethylene do inhibit it.

But, however the rôle of inhibitor may be divided between the carbide and adsorbed olefine hydrocarbons, the general result remains, that when carbide on the surface of the catalyst is attacked by molecular hydrogen Fischer oils are formed, and when it is attacked by chemi-sorbed hydrogen, the reduction is carried further and methane is produced. The mechanism of the formation, growth and final desorption of the long chain products can now be understood in the light of this result and of the following considerations.

3. The Hydrogenation-Cracking of Hydrocarbons on a Fischer Catalyst at 200° C.

As the carbon atoms in cobalt carbide occur separated, reduction of the carbide will lead first to separated $=CH_2$ groups chemi-sorbed on the cobalt. In the presence of chemi-sorbed hydrogen these are reduced immediately to methane, but in its absence they link up to form long paraffin chains. This conception of the long chains being built up from initially separated $=CH_2$ groups is demanded by the fact that the carbon atoms in these carbides are known to occur separated, and also by the fact that long chain hydrocarbons can be formed when carbides are reduced by dilute acids. Because in this latter case the growth of the long chains by steps, involving the alternate reaction of carbon-monoxide and then hydrogen at one end of the chain, is impossible as no carbon monoxide is present.

At this stage therefore one may either assume that the long chains formed by polymerisation of the methylene groups are chemi-sorbed as (I), or, instead, a rather more general picture, involving fewer assumptions, may be more satisfying, namely, that a catalyst surface containing a large number of CH_2 groups adsorbed on it, should be considered neither as (II) nor as (III)



but rather as (IV). In fact it may be considered to be a giant molecule, from which, by suitable treatment, fragments may be broken off. Thus experiments were performed to see how paraffin hydrocarbons are adsorbed and desorbed from a Fischer catalyst.

Ethane, propane and butane, mixed with the requisite amount of hydrogen were put in contact with a freshly reduced Fischer catalyst, and they all reacted at 200° C. to give methane. These reactions occur at rates comparable with the rate of formation and reduction of carbide, and hence at rates comparable to the Fischer synthesis. This is seen from curve (1) of Fig. 3 which was obtained when propane and hydrogen were put in contact with the catalyst at 200° C. In the case of butane and propane, a little ethane was detected in the final gases, but this was merely an intermediate stage in the formation of methane.

When the same hydrocarbon gases were then put in contact with the freshly reduced catalyst without adding any hydrogen, a reaction occurred in all cases at much the same rate as before, to give methane and to leave either carbon or CH or CH₂ radicles chemisorbed on the catalyst. Curves 2, 3 and 4 show the rate of this reaction for ethane, propane, and butane

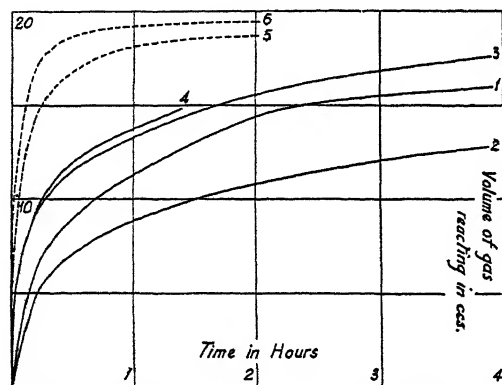


FIG. 3.—Rates of hydrogenation-cracking of paraffin hydrocarbons.

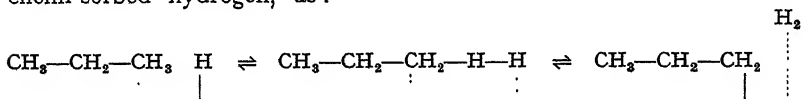
respectively. The carbon, or other radicles left on the catalyst was detected by pumping off the gaseous products of the reaction and then adding hydrogen, when methane was formed. Curves (5) and (6) show this reduction of the catalyst after the cracking of propane and butane respectively.

Unfortunately it is impossible to obtain a sample of catalyst free from hydrogen to begin with, because the necessary reduction of the cobalt oxide always

leaves hydrogen very firmly adsorbed on the surface, and this hydrogen can only be pumped off at temperatures so high as to ruin the catalyst completely. For the experiments described, the hydrogen was pumped off for several hours at 375° C. after the reduction, so that in all these cases it is certain that chemisorbed hydrogen was present initially.

When one of the hydrocarbon gases is put in contact with the catalyst at 200° C. and no hydrogen is added, an indefinitely large amount of the hydrocarbon is not cracked, but the reaction comes eventually to a standstill. For example, the 9 g. of catalyst used in these experiments would never react with more than 30 c.c. propane, to crack it to give 60 c.c. methane and the corresponding amount of carbon. This may be expressed differently by saying that a catalyst containing much carbon will not cause cracking, and this was proved in another way by putting propane in contact with a catalyst at 200° C. that had previously been converted into carbide by treatment with carbon monoxide. Again no reaction occurred. In both these cases the surface of the catalyst is free from chemisorbed hydrogen. And again, the reaction of paraffin hydrocarbons with hydrogen to give methane must be inhibited during the Fischer synthesis, otherwise no long chain compounds would be produced, and this is parallel to the inhibition of the ortho-para hydrogen conversion, and means that the hydrogenation-cracking of paraffin hydrocarbons at 200° C. needs chemisorbed hydrogen and will not work with molecular hydrogen.

Since therefore under all the conditions for which the dissociation of carbon-carbon bonds in hydrocarbons occurs at low temperatures, such as 200° C., chemi-sorbed hydrogen is present, and since, conversely, such dissociation does not occur in the absence of chemi-sorbed hydrogen during the Fischer synthesis, it is suggested that the dissociation is caused by attack of the hydrocarbon by chemi-sorbed hydrogen; or more precisely, by attack of the hydrocarbon which has previously been chemi-sorbed on the catalyst surface with its carbon-carbon bonds intact. Even this initial adsorption may be caused by the action of chemi-sorbed hydrogen, as:



These views are in contrast to the ideas of Taylor¹¹ who has examined the hydrogenation-cracking of ethane and propane on a nickel catalyst and who supposes that after the initial chemi-sorption of the hydrocarbon as described above, a dissociative adsorption occurs next, with rupture of the carbon-carbon bonds, and that only after this, the fragments react with hydrogen to give methane.

Accepting the view, therefore, that the presence of atomic, chemi-sorbed hydrogen leads to the rupture of carbon-carbon bonds in hydrocarbons adsorbed on the catalyst surface, and remembering the result of the *ortho-para*-hydrogen conversion experiments, that in the presence of much chemi-sorbed hydrogen, methane is produced from carbon monoxide and hydrogen instead of long chain hydrocarbons, it follows that in the Fischer synthesis, the breaking off of paraffin or olefine chains from the catalyst surface, or the disrapture of fragments from the giant molecule of CH₂ groups on the surface, is due to attack by chemi-sorbed hydrogen. If this latter were completely absent, paraffin waxes of an indefinitely large molecular weight would be produced. If only a little is present, long chain hydrocarbons will be formed, but if much is present methane will be the sole product.

4. The Incorporation of Ethylene into the Fischer-Tropsch Synthesis.

Under the conditions of the Fischer synthesis, carbon monoxide has a bigger affinity for the catalyst surface than any of the other components, so that the effect of introducing ethylene into the reacting system might be very instructive, because it has an equally great affinity for the metal surface, and, being a reactive hydrocarbon as well, it might probably take an active part in the reaction. Smith, Hawk, and Golden¹² did experiments by passing ethylene, carbon monoxide and hydrogen over a Fischer catalyst, and their results have been confirmed and in one direction extended by the present work. They used a cobalt-copper-manganese oxide catalyst at 204° C., and found that while some of the ethylene was simply hydrogenated to ethane, some was incorporated in the Fischer reaction to give oils (Table V). They also found that when ethylene is incorporated the products contain up to 50 per cent. of oxygen compounds such as alcohols, aldehydes, etc.

¹¹ K. Morikawa, W. S. Benedict, and H. S. Taylor, *J.A.C.S.*, 1936, **58**, 1795; K. Morikawa, N. R. Trenner, and H. S. Taylor, *ibid.*, 1937, **59**, 1103.

¹² D. F. Smith, C. O. Hawk, and P. L. Golden, *ibid.*, 1930, **52**, 3221.

TABLE V.

Gases passed over Catalyst (litres).				C_2H_4 Reacting (litres).	C_2H_4 Formed (litres).	Oil Formed, gms. (above C_4H_{10}).
H_2	CO	C_2H_4	N_2			
78	67	81	—	52	40.5	12.7
79	66	—	84	—	0.3	3.3

The present work confirmed these results, using the standard cobalt-thoria-kieselguhr catalyst, and also showed that although under the normal conditions this catalyst will yield no oil at $280^\circ C.$, but methane only, yet in the presence of ethylene there was a copious yield of oil. In the actual experiment a mixture of $CO + 2H_2 + C_2H_4$ was passed over the catalyst and the gases reacted in the proportions: H_2 1.70 : CO 0.94 : C_2H_4 0.94. The carbon monoxide would take at least (0.94×2) litres of hydrogen, thus leaving none for the hydrogenation of the ethylene. This has therefore been incorporated in the reaction products of the carbon monoxide and hydrogen. It should also be stated that blank experiments proved that ethylene alone, or mixed with carbon monoxide passes unchanged over the Fischer catalyst under these conditions, and ethylene mixed with hydrogen gives ethane only, no higher hydrocarbons being detected.

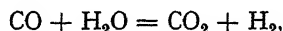
The result that in the presence of ethylene oils can be synthesised at $280^\circ C.$ is easily explained and supports the general contention that methane is only formed in the presence of chemi-sorbed hydrogen. Because ethylene, both by its strong adsorption and by its reactivity, will reduce the concentration of chemi-sorbed hydrogen on the catalyst surface very largely, and will therefore lead to the production of oils under conditions where, in the absence of the ethylene, only methane could be formed.

The result of Smith, Hawk and Golden that the presence of ethylene leads, moreover, to the production of organic oxygen-containing compounds recalls the well-known fact that increasing the pressure during a normal Fischer reaction changes the character of the products, more and more oxygen compounds being formed as the pressure is increased. Furthermore, it suggests an explanation for both. The experiments on the *ortho-para*-hydrogen conversion have shown that the normal Fischer reaction is primarily the reaction of molecular hydrogen, that is, of hydrogen not directly in contact with the surface of the catalyst, with chemi-sorbed carbon monoxide and carbide on the surface. The initial effect of a large amount of ethylene added artificially would undoubtedly be a competition with the carbon monoxide for the catalyst surface, with the result that the usual high surface concentration of chemi-sorbed carbon monoxide and carbide will not be maintained, and carbon monoxide will be adsorbed, as such, in the second adsorption layer, without being in contact with the surface. And it is rather likely that reactions of carbon monoxide adsorbed in this feebler way are such as to leave the oxygen as part of the resulting molecule. This explanation fits in with the effect of increasing the pressure, because an increase of pressure can have no big effect on the amount of substances chemi-sorbed on the catalyst surface, because that will depend rather on the available space on the surface. Thus a reaction depending only on the chemi-sorbed layer should not change radically on increasing the pressure. But an increase of pressure will increase very largely the amount of substances adsorbed by the feebler forces in the second and

outer adsorption layers. In the case of the reaction of carbon monoxide with hydrogen an increase of pressure causes the appearance of a completely new type of compound, namely the organic substances containing oxygen, so that it seems very likely that these are formed by reactions involving carbon monoxide held in the other adsorption layers.

5. The Water-Gas Shift Reaction.

It is well known that cobalt preparations are the most active catalysts for the water-gas shift reaction,



which at low temperatures such as 200° C. should proceed almost completely from left to right. Yet the oxygen product from the Fischer reaction is water only, the amount of carbon dioxide formed during synthesis with a cobalt catalyst being very small indeed. But when conditions are altered to lead to the synthesis of methane instead of oil, as, for example, by raising the temperature to 250°-300° C., the water-gas shift reaction appears to set in, as much of the water becomes replaced by carbon dioxide. From these observations it follows that water is the primary oxygen product of the Fischer reaction, that during the Fischer synthesis the water-gas shift reaction is inhibited, just like the *ortho-para*-hydrogen conversion and the hydrogenation cracking of paraffin hydrocarbons, and that when the synthesis of methane is taking place, the water-gas shift reaction can again occur, like the *ortho-para* hydrogen conversion and the hydrogenation-cracking reactions.

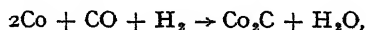
Summary of Experimental Results.

1. At the temperature of the Fischer synthesis, carbon monoxide reacts slowly with the Fischer catalyst to give cobalt carbide, as



but this reaction is always slower than the reduction of the carbide by hydrogen at the same temperature.

2. At this temperature the catalyst reacts with carbon monoxide and hydrogen to give carbide as,



and this reaction is faster than the reduction of the carbide by hydrogen under the synthesis conditions.

3. Reduction of cobalt carbide may lead to methane or to higher hydrocarbons, according to the conditions, and the experiments have shown that when oils are being produced by the Fischer synthesis, the *ortho-para*-hydrogen conversion is inhibited, showing that very little chemi-sorbed hydrogen occurs on the catalyst surface.

4. Under all the varied conditions for which methane is the product of the synthesis instead of oil, the *ortho-para*-hydrogen conversion occurs freely, showing that chemi-sorbed hydrogen is then present.

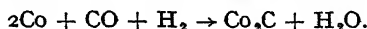
5. The water-gas shift reaction runs parallel to the *ortho-para*-hydrogen conversion; it occurs when methane is being formed, but is inhibited during oil formation by the Fischer synthesis.

6. The hydrogenation-cracking of paraffin hydrocarbons on the Fischer catalyst is similarly inhibited during the Fischer synthesis, and also by the presence of carbide on the catalyst surface, but otherwise it occurs freely at similar temperatures.

7. If ethylene is added to the reacting gases during the Fischer synthesis it becomes incorporated in the products but it leads simultaneously to the formation of organic substances containing oxygen, such as alcohols, acids, etc.

Summary of Theoretical Deductions.

1. The first step in the Fischer synthesis is the alternate formation and reduction of cobalt carbide to give CH_2 groups, the carbide being formed by the reaction



2. In the presence of chemi-sorbed hydrogen, these methylene groups are further hydrogenated to methane.

3. When the conditions are such that the formation of carbide is more rapid than its reduction, there will be very little chemi-sorbed hydrogen on the surface, and the CH_2 groups will link up to give long chains.

4. The products actually obtained are broken off the long chains on the surface by attack of chemi-sorbed hydrogen.

5. When carbon monoxide is adsorbed in the outer adsorption layers and not in direct contact with the catalyst surface its reduction leads to compounds containing oxygen, rather than hydrocarbons.

This work, which forms part of the programme of the Fuel Research Board of the Department of Scientific and Industrial Research, has been carried out in the Department of Colloid Science, Cambridge, under the supervision of Professor Rideal, to whom the writer is indebted both for suggesting this research and for constant advice during its progress. This account is published by permission of Dr. F. S. Sinnatt, Director of Fuel Research.

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EXPERIMENTS ON THE FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN.

BY E. F. G. HERINGTON AND L. A. WOODWARD.

Received 6th February, 1939.

In the Fischer-Tropsch synthesis,¹ which has been developed on an industrial scale in Germany, paraffin and olefine hydrocarbons ranging from the lightest members up to solid waxes are simultaneously produced from carbon monoxide and hydrogen. The reaction takes place in the presence of promoted iron, cobalt and nickel catalysts at atmospheric

¹ F. Fischer and H. Tropsch, *Ber.*, 1926, 59, 830, and numerous subsequent papers in *Brennstoff-Chemie*. For a recent review by Fischer see *Ber.*, A, 1938, 71, 56.

pressure and at temperatures in the neighbourhood of 200° C. The experiments described in this paper were carried out in continuous laboratory-scale apparatus using from 15 to 75 g. of catalyst.

A catalyst of composition corresponding to Co : ThO₂ : kieselguhr = 100 : 18 : 100 by weight was used throughout. It was prepared from the nitrates by precipitation of the carbonates in the manner previously described.² The catalyst, which was in the form of pellets, was in every case given a preliminary reduction in hydrogen for twenty-four hours at 350° to 375° C.

1. Reaction Producing no Liquid or Solid Hydrocarbons.

We have observed that occasionally a sample of catalyst fails to produce liquid or solid hydrocarbons under the normal conditions of ingoing gas composition, space velocity and reaction temperature, although water is formed and the catalyst is active as judged by gas contraction.* Other samples of the same batch preparation of catalyst may behave normally.

In one experiment no oil was produced after 72 hours' running at 195 C., although the gas contraction was over 50 per cent. throughout. The analysis of a sample of the effluent gas at the end of this period (gas contraction 52 per cent.) was as follows: C_nH_{2n+2}, 31.8 per cent.; n = 1.16; CO, 0.3 per cent.; CO₂, 12.9 per cent. The ingoing gas had H₂/CO = 2.8 and contained 2.4 per cent. of CO₂. The low n value of the saturated hydrocarbons in the effluent gas indicates that the principal hydrocarbon product was methane.

Further experiments showed that such failure to produce higher hydrocarbons is caused by not lowering the catalyst temperature sufficiently (after the initial catalyst reduction) before admitting the carbon monoxide-hydrogen mixture, or by raising the temperature too rapidly to synthesis temperature. It is also favoured by a high H₂/CO ratio in the ingoing gas (see Section 2 below).†

For convenience we may use the general term "methane reaction" in referring to such failure of an active catalyst to produce liquid or solid hydrocarbons. Besides the predominant production of methane, the following properties of the behaviour in question were observed:—

(1) When synthesis gas with the optimum H₂/CO ratio for oil production (*i.e.* 2) is being used, excessive amounts of CO₂ are produced (*e.g.* from 15 to 25 per cent. in the effluent gas).

(2) The extent of the reaction, as measured by the percentage gas contraction, is not so sensitive to temperature variations as during oil synthesis.

(3) The volume contraction rarely exceeds 60 per cent.

(4) Water is produced, but no oil.

A further interesting characteristic is that the carbon dioxide content of the effluent gas depends on the H₂/CO ratio of the ingoing gas, being

* *Annual Report of the Fuel Research Board*, 1937, p. 145; 1938, p. 189.

* The percentage gas contraction over a suitable period

$$\left(\frac{\text{vol. of ingoing gas} - \text{vol. of effluent gas}}{\text{vol. of ingoing gas}} \times 100 \right)$$

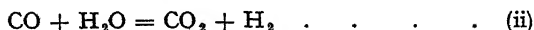
forms a convenient measure of the extent of reaction.

† The H₂/CO ratio of 2.8 in the experiment referred to above is admittedly higher than is usually employed in the Fischer-Tropsch synthesis (optimum H₂/CO ratio = 2). As was shown by other experiments, however, a ratio of 2.8 is by no means incompatible with the production of oil, provided that the catalyst is suitably "run in" (see below).

lower for higher values of the ratio. This suggests that with H_2/CO ratios greater than 3 the CO is almost entirely removed by the reaction

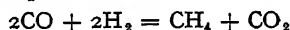


whereas with lower H_2/CO ratios (*i.e.* with more CO than is required for reaction (i)) some of the water produced by reaction (i) may react with the excess CO according to



Both of these reactions are known to occur on a cobalt catalyst.

Evidence that the "methane reaction" involves such a consecutive occurrence of reactions (i) and (ii) was obtained from observations during the initial period after admitting synthesis gas (H_2/CO ratio nearly 2) to a freshly reduced catalyst at $195^\circ C$. The temperature was kept constant throughout and no oil was produced. The results, which are represented in Fig. 1, may be explained as follows. For a gas with $H_2/CO = 2$ the maximum percentage contraction possible by reaction (i) alone is $66\frac{2}{3}$, whereas by the combined reactions (i) and (ii) according to the equation



it is $33\frac{1}{3}$. Hence, the fact that the observed contraction passed through a maximum (see graph 1a) indicates an initial lag of reaction (ii) behind reaction (i), and so provides evidence of their consecutive character. This is confirmed by comparison with graph 1b, which shows that the amount of CO_2 produced, which is a measure of the extent of reaction (ii), was still small at the time of maximum gas contraction, and subsequently increased as the contraction fell.

Experience has shown that oil synthesis can be ensured by "running in" the catalyst in a suitable manner. The temperature should be well below $150^\circ C$.

when synthesis gas is first admitted in place of hydrogen. The temperature should then be raised very slowly, a satisfactory procedure being to hold the temperature constant for 2 hours, when the contraction reaches 20 per cent., then again constant for two hours at 30 per cent., 40 per cent. and so on. In this way it has been found possible to induce oil formation on any sample of active catalyst.

Even in the case of a sample of catalyst which had given the "methane reaction" owing to unsatisfactory "running in," it was found possible to induce oil formation by lowering the temperature and following out the "running in" procedure described above. The striking effect of this treatment is apparent from a comparison of the analyses of the effluent gases in Table I.

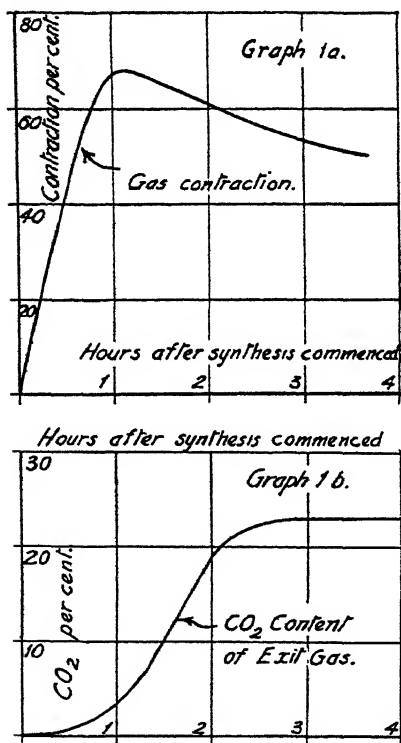
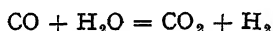


FIG. 1.—Reaction producing no liquid or solid hydrocarbons.

The effluent gas sampled during the "methane reaction" has a high percentage of saturated hydrocarbons of low n value, a high percentage of CO_2 and a low percentage of CO . It stands in marked contrast to the effluent gas sampled during the oil synthesis which followed suitable "running in" of the same catalyst.*

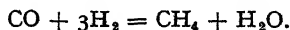
Once oil synthesis has been induced, no difficulty is experienced in maintaining it. We thus have the observation that one or other of two reactions, the "methane reaction" or oil synthesis, may persist on the catalyst under the same conditions of ingoing gas composition, space velocity and temperature. There is evidence from the work of Fischer and others that carbide is present during oil synthesis, and Craxford³ has shown that the *ortho-para* hydrogen conversion takes place only to a small extent. On the other hand, the "methane reaction" is such as might be expected for a bare metal surface. Thus the production of more CO_2 than during oil synthesis may be due to the reaction



having a greater rate on the bare metal than on the carbide. In accordance with this, the *ortho-para* conversion is found by Craxford to proceed in all cases when no oil is being synthesised. The "running in" procedure which is found to prevent the "methane reaction" may therefore be connected with the formation at the lower temperatures of carbide which then persists during the Fischer-Tropsch synthesis.

2. Effect of High H_2/CO Ratio in the Ingoing Gas.

Under otherwise similar conditions of reaction, a high H_2/CO ratio in the ingoing gas favours the formation of hydrocarbons of lower molecular weight. Thus an experiment carried out with a gas having the H_2/CO ratio 8.44 failed to produce any liquid or solid hydrocarbons, although the "running in" and reaction conditions were such as would have ensured oil synthesis with a normal synthesis gas having H_2/CO equal to 2. The observed gas contraction corresponded approximately to the maximum possible for the reaction



Although the experiment was continued for over 200 hours, and considerable quantities of water were collected, no oil was produced. At the end

* In Table I the temperature of oil synthesis is lower than that of the initial failure to produce oil. This difference is not sufficient, however, to account for the difference of products; for other experiments have shown that, when once oil synthesis has commenced, a rise of temperature from 185°C . to 197°C . will neither stop oil formation nor cause such a marked increase in the amounts of CO_2 or saturated hydrocarbons in the exit gas.

³ S. R. Craxford, preceding paper.

TABLE I.—EFFLUENT GAS SAMPLES.

	"Methane Reaction."	During Oil Synthesis.
Reaction Temp.	197.	184.
Percentage Gas Contraction.	59.	54.
CO_2 . . .	22.8	9.9
CO . . .	0.3	14.6
$\text{C}_n\text{H}_{2n+2}$. . .	43.1	10.4
n . . .	1.10	1.89

(The ingoing gas had $\text{H}_2/\text{CO} = 2.3$ and contained 3.0 per cent. of CO_2 .)

of the experiment the catalyst was removed and extracted in a Soxhlet apparatus, but no hydrocarbons were found in it.

These results are in harmony with those of Craxford,³ who has found that with high H_2/CO ratios the predominant hydrocarbon product at 200° C. is methane.

3. "Dewaxing" with Hydrogen.

After a catalyst has been in use for some time, a remarkable revivification effect can be obtained by passing hydrogen over it for a short time at synthesis temperature.⁴ This treatment, which may be conveniently referred to as "hydrogen dewaxing," seems to owe its efficacy to a partial removal of high-boiling waxy products which were previously cloaking the catalyst surface and so impairing its activity.

The experiments about to be described were carried out in order to find whether the effect of hydrogen is purely physical or whether it involves a specific chemical interaction.

A batch of catalyst was run for 7½ days in the normal manner, at the end of which time it was giving 110 g. of liquid product per cu. m. of ingoing gas, the contraction being 60 per cent. and the temperature 192° C. In order that any increases of activity due to dewaxing treatments should be as easily detectable as possible, the temperature was lowered until the contraction was 45 per cent. The temperature, which was then 184° C.,

TABLE II.

Treatment of Catalyst.	Duration Hrs.	Yield of Liquid Hydrocarbons, (g. per cu. m. of Ingoing Gas).
Synthesis after 7½ days' running .	12	57.2
Passing nitrogen .	3½	—
Synthesis after pass- ing nitrogen .	17	61.2
Passing hydrogen .	3½	—
Synthesis after pass- ing hydrogen .	15	75.5

was kept steady while the successive treatments described in Table II were carried out. The rate of input of gas was the same throughout.

After the treatment with hydrogen a burst of high activity was observed on admission of synthesis gas, the contractions rising transiently to 75 per cent. We have observed this phenomenon repeatedly in larger-scale working, where continuous recording of the CO_2 content of the effluent gas has shown that the

transitory high activity is associated with excessive production of CO_2 . No such effect as this was observed after the treatment with nitrogen. The final test period of 15 hours' synthesis was started after the transitory high activity had partially passed away and the contraction had fallen to 65 per cent. During the first four hours of this test period the contraction fell to about 53 per cent., at which it remained practically constant. The average contraction over the fifteen hours was 57½ per cent. Thus the treatment with hydrogen, unlike the treatment with nitrogen, had a marked effect in raising the activity and the yield of liquid hydrocarbons.

The treatments described in Table II were repeated, but the nitrogen and hydrogen were passed for twelve hours instead of three and a quarter.

⁴ British Patent No. 486,929.

The results obtained were similar to those already described, the effect of the hydrogen being much more pronounced than that of the nitrogen.

The results of both experiments are summarised in Table III.

TABLE III.

Duration of Passage of N ₂ or H ₂ during Treatment.	Ratio of Liquid Hydrocarbon Yield after Treatment to Yield before Treatment.	
	N ₂ .	H ₂ .
3½	1.07	1.23
12	1.12	1.24

It is significant that during the passage of nitrogen over the catalyst no appreciable gas contraction could be observed, whereas during the passage of hydrogen a small but definite contraction was apparent. From this it may be concluded that most of the revivifying effect of the hydrogen is due to chemical interaction, whereas the relatively slight effect of nitrogen is probably to be attributed to a purely physical removal of a small quantity of product from the catalyst surface.

4. The Effect of Sulphur Compounds upon the Catalyst.

According to Fischer⁵ the catalysts used in the synthesis of liquid hydrocarbons from carbon monoxide and hydrogen are readily poisoned by sulphur compounds, so that for satisfactory running it is necessary to reduce the sulphur content of the ingoing gases to an extremely low figure. The following experiments were carried out in order to investigate more closely the effect of sulphur compounds.

There is evidence that during the Fischer-Tropsch synthesis the greater part of the catalyst surface is carbided, and it seemed possible that the first traces of sulphur might combine preferentially with the uncarbided portions of the surface. If this occurred, it might affect preferentially those partial reactions which involve the agency of adsorbed hydrogen; for in view of the work of Craxford on the *ortho-para* hydrogen conversion, it is upon the uncarbided portions of the surface that the adsorption of hydrogen would be expected to occur.

A sample of the standard catalyst was first "run in" with pure synthesis gas (H₂/CO = 2) and then H₂S was admitted with the synthesis gas in regulated discontinuous amounts by dissolving weighed pellets of cadmium sulphide in hydrochloric acid in a bubbler included in the ingoing gas line. Throughout the experiment no H₂S passed out of the catalyst tube in the effluent gases. A small glass reaction vessel was used (weight of catalyst 15 g.), and no attempt was made to collect all the liquid products. The effluent gases passed through a bubbler containing water, in which the higher-boiling oil condensed. Thus the products were virtually fractionated; the heavier condensate was collected and measured, and the lighter hydrocarbons in the gas passing through the bubbler were determined by analysis of snap samples. The yields, in each case relative to the corresponding yields before addition of sulphur, are given in Table IV.

The additions of sulphur did not seriously poison the catalyst. The relatively high resistance to sulphur poisoning exhibited in Table IV is similar to that observed by Japanese workers⁶ for Ni-Mn catalysts used

⁵ See, for example, F. Fischer, *Brennstoff-Chemie*, 1935, 16, 5.

⁶ K. Fujimura, S. Tsuneoka, and K. Kawamichi, *J. Soc. Chem. Ind. Japan*, 1934, 37 (7), 395B.

for the Fischer-Tropsch synthesis. These workers record the total yield of liquid hydrocarbons, whereas in Table IV the relative yields of heavier and lighter fractions are given. The interesting fact emerges that the first additions of sulphur cause a marked increase in the yield of the heavier

TABLE IV.

Amount of Sulphur Added.	Catalyst Temperature.	Ratio of Hydrocarbon Yields to Corresponding Yields before Addition of Sulphur.	
Mg. per g. of Catalyst.	°C.	Condensed Oil.	Hydrocarbons in Effluent Gas ($n = 1.7$).
0.00	183	1.00	1.00
0.67	183	2.3	1.0
3.50	183	2.1	0.8
7.94	183	—	0.5
7.94	195	2.0	1.3
13.4	195	1.5	—
33.5	207	1.2	2.1

fraction at constant reaction temperature. As to the lighter hydrocarbons, there is a diminution with progressive addition of sulphur; but for small quantities of sulphur this is not so marked as the increase in the heavier fractions, so that, in agreement with the findings of the Japanese workers,⁶ the total hydrocarbon yield is slightly enhanced.

In the preceding paper by Craxford the idea is put forward that the observed hydrocarbon products leave the catalyst surface owing to the fragmentation of macro-molecules by the agency of chemisorbed hydrogen. Alternatively the liberation of the chains from the surface may be due to saturation of the previously unsaturated molecules by hydrogen, a process which will also be expected to occur preferentially on the bare metallic centres. On either theory the effect of sulphur in displacing the distribution of the hydrocarbon products in the direction of higher molecular weights is consistent with the view that the sulphur preferentially poisons those catalyst centres where the liberation of the observed products is effected.

Continued addition of sulphur at constant reaction temperature causes a diminution of total activity and a consequent falling off of yield, but this can be offset by raising the reaction temperature rather more rapidly than would normally be necessary. This is also illustrated in Table IV. The higher temperatures favour the production of lighter hydrocarbons; but even so, after the addition of as much as 33.5 mg. of sulphur per g. of catalyst, the yield of condensed oil could still be maintained higher than before the addition of sulphur.

In another experiment similar amounts of sulphur were added in the form of carbon disulphide by entrainment in the synthesis gas. Again an enhancement of the production of hydrocarbons of higher molecular weight was observed.

The experiments described above were carried out in the normal Fischer-Tropsch range of temperature. A similar effect was observed in experiments carried out at 300° C., at which temperature the predominant hydrocarbon produced in the absence of sulphur is methane. We have seen above that a high value of the H_2/CO ratio of the ingoing gas favours the production of hydrocarbons of lower molecular weight. Experiments on the admission of sulphur compounds were carried out with H_2/CO

ratios of 1.4 and 3.5. In both cases the sulphur had the effect of raising the n value of the effluent hydrocarbon gases (C_nH_{2n+2}), the rise being more marked in the experiment with the lower H_2/CO ratio in the ingoing gas. In this case the n value rose from less than 1.1 to 1.3 after the addition of approximately 2 mg. of sulphur per g. of catalyst, whereas when the H_2/CO ratio in the ingoing gas was 3.5 the same rise of n value did not occur until approximately 10 mg. of sulphur per g. of catalyst had been added. In the experiment with $H_2/CO = 1.4$ the catalyst, after "poisoning," actually produced heavy liquid hydrocarbons at 300° C.

Experiments were also carried out at 350° C. with H_2/CO ratios of 2.4 to 3.5. At this temperature the hydrocarbon product was almost entirely methane and no appreciable increase of n value could be observed for additions of sulphur up to as much as 65 mg. of sulphur per g. of catalyst. This effect of raising the reaction temperature is to be expected on the view that the formation of the longer chains is associated with the presence of surface carbide. Bahr and Jessen,⁷ working on the reaction of CO with unpromoted cobalt, showed that at 290° C. the percentage of carbide present was 3.4, whereas at 340° C. it was only 0.3. At 350° C., therefore, the amount of carbide which can exist on the catalyst surface is presumably insufficient for the formation of any but the lightest hydrocarbons, even though sulphur is added.

Reverting now to synthesis carried out in the normal Fischer-Tropsch range of temperature, experiment showed that the toxic effect of sulphur does not depend only upon the quantity added, but also upon the thermal treatment of the catalyst. Thus, a sample of catalyst was run at about 200° C. on gas ($H_2/CO = 3.2$) containing organically combined sulphur. Initially a contraction of 59 per cent. was observed. By the time 19.4 mg. of sulphur per g. of catalyst had been admitted, the contraction had sunk to 38 per cent. and the yield of oil had fallen off correspondingly. At this point the synthesis gas was purged out of the catalyst vessel with pure hydrogen, after which the temperature was raised to 375° C. and the catalyst was kept at this temperature for fourteen hours in a stream of hydrogen. It was hoped that this treatment might remove some of the sulphur and so effect a revivification of catalyst activity. However, no H_2S was observed to leave the tube; and the catalyst, when tested subsequently with synthesis gas at 200° C., gave only 10 per cent. contraction.

It was shown by other experiments that similar treatment of an unpoisoned catalyst with hydrogen at 375° C. does not impair its activity. In seeking an explanation of the marked effect in the case of the catalyst containing sulphur, it is to be borne in mind that the action of the hydrogen at 375° C. will clear the catalyst surface of carbide or other protection. The observed increase of toxicity may possibly be due to a redistribution of the sulphur, resulting in the poisoning of very active centres which were previously protected by carbide or in some other way. A similar effect has been reported by Fischer.⁸

It must not be supposed that the catalyst cannot be completely poisoned during reaction at 200° C. by sulphur compounds contained in the ingoing gas. Experiment showed that the passage of excess H_2S or CS_2 over the catalyst, either before or during synthesis, resulted in complete loss of activity. A sample of catalyst which had been completely poisoned in this way showed on analysis a ratio of cobalt to sulphur equal to 70.6 : 29.4 by weight. (Theoretical for Co_3S_2 , 73.4 : 26.6; for CoS , 64.6 : 35.4.)

5. General Conclusions as to Reaction Mechanism.

The experimental results reported above are consistent with the view that during the Fischer-Tropsch synthesis the catalyst surface possesses centres of two types: Type A (probably cobalt carbide) which is responsible

⁷ H. A. Bahr and V. Jessen, *Ber.*, **B**, 1930, 63, 2227.

⁸ F. Fischer, *Ges. Abh. Kenntnis Kohle*, 1930, 10, 469.

for the formation of the CH_3 groups whose polymerisation leads to the production of long chain hydrocarbons; and Type B (probably bare cobalt metal) which is responsible through the agency of hydrogen for the liberation of the observed products from the catalyst surface.

One or other of two reactions may persist on the catalyst at the same temperature. During the first reaction, when (besides water) only gaseous products are formed, centres of Type B predominate over those of Type A; whereas during the Fischer-Tropsch synthesis, when liquid and solid hydrocarbons are produced, the reverse is true. The "running in" procedure which may be adopted to avoid the first reaction allows of the plentiful formation of centres of Type A, which then persist during synthesis. In the revivification of the catalyst by treatment with hydrogen, products of high molecular weight are removed from the surface of the catalyst by chemical interaction of the hydrogen, a process presumably similar to that by which the observed products are liberated from the surface during synthesis. On the surface thus cleared by hydrogen excessive quantities of gaseous products are transitorily formed, presumably owing to the presence of more centres of Type B than are present during normal synthesis.

The addition of sulphur compounds during the Fischer-Tropsch reaction at first causes an increased production of hydrocarbons of higher molecular weight, an effect which may be explained by assuming that the sulphur preferentially poisons the centres of Type B. Treatment with hydrogen at 375°C . destroys the preferential sulphur resistance of centres of Type A, so that with a partially poisoned catalyst there may be a redistribution of the sulphur resulting in an increased degree of poisoning for the Fischer-Tropsch synthesis.

This work formed part of the programme of the Fuel Research Board of the Department of Scientific and Industrial Research, and the above account is published by permission of Dr. F. S. Sinnatt, Director of Fuel Research.

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*Fuel Research Station,
Greenwich.*

GENERAL DISCUSSION.*

Prof. W. E. Garner (*Bristol*) said: Craxford has drawn attention to the possibility that CH_3 groups attached to the metal atoms of the catalyst form an intermediate stage in the production of hydrocarbons. In order that hydrocarbons be formed from scattered methylene groups, some mobility over the surface is necessary. This might occur by the movement of the CH_3 groups themselves, which entails the breaking of the carbon-metal bond, or could be brought about by the surface diffusion of the metal atoms to which the CH_3 groups are attached.

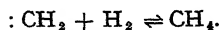
Evidence has been obtained of the existence of such surface movements in the adsorption of CO on oxides. This adsorption occurs in two stages: (1) with the liberation of 20-30 K.cal., which is probably chemisorption, with the production of unsaturated linkings on the surface, and (2) the disappearance of the unsaturation with the liberation of 30-40 K.cal. In the case of some oxides these two processes occur simultaneously. The energy yielded by the disappearance of the unsaturation, may be of importance in certain cases in determining whether or not one mechanism

* On the two preceding papers.

is preferable to another (*e.g.*, the reaction between hydrocarbons and deuterium).

It is felt that in the discussion of the mechanism of catalytic processes, sufficient attention is not paid to the movements of the atoms of the absorbent.

Prof. M. W. Travers (*Bristol*), called attention to the results of an investigation published in the *Transactions* last year which showed that the long-continued action of hydrogen on carbon at comparatively low temperatures appeared to result in the formation of methylene groups around the edge of the lattice, and to the establishment of a pseudo-equilibrium represented by



SECTION B. HYDROGENATION REACTION OF COAL AND LIGNITE.

ON THE REACTIONS OF THE CATALYTIC HIGH-PRESSURE HYDROGENATION OF COAL AND OIL AND THEIR CONTROL.

By M. PIER.*†

Received in German on 6th February, 1939, and translated by C. BONDY.

Various catalytic processes for the production of low-boiling hydrocarbons have been developed in the course of time apart from the purely thermal processes used exclusively in the past. The catalytic high-pressure hydrogenation of coal and oil has become of great practical importance for Germany, a country which is poor in petroleum but rich in coal. Technology was faced with the difficult task of producing petrol as well as other refined products, such as illuminating oils, Diesel oils, lubricating oils, paraffins and fuel oils from bituminous coal, brown coal, peat, pitch, high- and low-temperature tars, oil shale and petroleum. Moreover, all this had to be done at a time when demands upon the quality of the products were constantly increasing.

This task was solved suitably by an *adaptation* of high-pressure hydrogenation to the various raw materials and to the desired properties of the final products. This adaptation was possible, because the reactions by which raw materials of so complex a nature as coal can be decomposed may, under different working conditions and with suitable control, proceed in many different ways.

The problem facing the industrial chemist was the investigation of these reactions, so as to facilitate or hinder them as required. The rules found in industrial high-pressure hydrogenation, though often not comparable with the elaborate and well-founded laws of exact science, are no less important and useful for work in this field. It was with their aid, and that alone, that the large-scale production of fuels was obtained.

The following are *the classes of chemical reactions* which play the most important part in the high-pressure hydrogenation:—

* High-pressure experiments of the *I.G. Farbenindustrie Aktiengesellschaft* carried out by the author and his collaborators.

† Presented by Dr. H. Fromherz (*Ludwigshafen/Rh.*)

1. Hydrogenation and dehydrogenation (addition and splitting-off of hydrogen).
2. Splitting, polymerisation and condensation (breaking and formation of C—C bonds).
3. Refining (splitting-off of oxygen, sulphur and nitrogen; reduction).

The combination of these fundamental reactions can be varied in many different ways; the splitting-off of oxygen is often in itself a combination of reduction (or hydrogenation) and the splitting-off of water. Purely *physical processes*, such as solution, adsorption, diffusion and distillation processes are, as a rule, inseparably and essentially connected with these chemical reactions.

The *working conditions* are characterised chiefly by the following factors: temperature, pressure, partial pressures of the reaction components, catalysts, contact period, stirring and manner of reaction control; liquid-phase or vapour-phase; solvent or pasting oil; re-cycle.

The cautious demolition of the complicated structure of coal with full utilisation of the valuable components and the improvement of the less valuable, these are the objects of catalytic high-pressure hydrogenation, and the reactions have to be designed accordingly.

General Points Concerning the Chemical Reactions.

The modes of interplay of these chemical reactions are as manifold as the nature of the desired hydrocarbons is varied. *Refining reactions* offer the best insight. Since as complete as possible an elimination of oxygen, sulphur and nitrogen is essential for most products, a refining reaction must, under all circumstances, be included in the decomposition process, at one stage at least, usually in the last one.

The exclusion of hydrogen causes undesirable *splitting and condensation reactions* to predominate. This is usually also the case where hydrogen is present but catalysts are absent. The main effect is a disproportionate redistribution of hydrogen. Products with low hydrogen content, such as coke, are formed from coal and oils by dehydrogenation, accompanied by polymerisation and condensation; whilst hydrogenation and splitting lead to products rich in hydrogen, such as petrol, liquefiable gases and, in extreme cases, methane. With regard to the cracking reactions it is interesting to note that breakdown to carbon and methane involves the greatest decrease of free energy; it is, therefore, thermodynamically the most probable reaction, and it follows, therefore, that in technical work the reactions must not be allowed to reach thermodynamic equilibrium. This is one of the reasons why it has been found necessary in carrying out experiments on this subject to ensure that the process is done continuously.

By the addition of highly compressed hydrogen and by the use of controlling catalysts one can emphasise the *hydrogenation and dehydrogenation reactions* to a greater or less extent, while inhibiting too far-reaching polymerisation and decomposition (gasification) which leads to coke and methane. Medium-length hydrocarbons of varying side-chains, cyclisation and saturation are thus favoured.

It is just this controlled competition between hydrogenation and dehydrogenation reactions on the one hand and splitting and polymerisation reactions on the other hand which is of fundamental importance for the final composition and properties of the decomposition products of coal. An anti-knock, and thus high-performance, petrol requires a high

aromatic content and strongly branched chains ; the reverse is true for a good Diesel oil, while a good lubricating oil needs comparatively simple ring systems with long side chains.

The Steps of the Reaction.

In order to master this diversity of competing reactions and of reaction products with contrasting properties, it has been found expedient, especially when starting from coal- or asphalt-containing raw materials of high molecular weight, to employ two stages of hydrogenation widely differing in their reaction character.

In *liquid-phase* treatment, coal or heavy oil residues are converted as far as possible to intermediate products, *viz.*, heavy and middle oils. This is assisted by small amounts of finely divided catalysts.

The main object of liquid-phase hydrogenation is the reduction and splitting of the originally present or newly formed asphalts to oils. This reaction can, in principle, also be carried out in presence of catalysts in high concentration. This procedure is, however, unsuitable for the treatment of ash-containing raw materials. It is also inexpedient, for instance, for the treatment of materials with a high asphalt content, especially when high temperatures are used for the sake of rapid conversion, because polymerisation reactions occur. Though the latter play but a small part, the products damage the activity of the catalyst. Only small amounts of catalysts are, therefore, used and these are passed through the converter along with the reaction materials. The time during which the catalysts stay in the converter need not, however, be only that of the reaction materials. For example, it is possible to increase this by sedimentation or re-cycle.

This procedure, suitably modified, may also be applied to raw materials with lower boiling-points or, under certain conditions, to completely volatile substances.

Liquid-phase splitting can be regarded as a normal thermal cracking reaction, so accelerated by the catalyst that back-polymerisation of unsaturated intermediate products to pitch and coke is prevented at the high-hydrogen pressure. From what has been said it is seen that the nature of the raw materials determines the liquid-phase products.

The manner of the introduction of hydrogen is of great importance, although it is not a factor which directly determines the reaction. Suitable stirring and mixing is necessary for effective distribution of hydrogen. It is assisted by the solubility of hydrogen in oils, which increases at higher temperatures. It is noteworthy that hydrogen is more soluble in oils rich in hydrogen than in oils containing little hydrogen and is but sparingly soluble in asphalts. Wherefore it is expedient to dilute asphalts with suitable oils previous to hydrogenation.

For the hydrogenation of coal it is necessary to depolymerise the solid matter to oil and to remove the residual coal which is difficult to hydrogenate and especially the ash constituents. It is immaterial, in principle, at which stage of the hydrogenation process the removal of these constituents takes place ; practical and economic considerations alone decide the order of these operations. One may either slightly depolymerise the coal first to high-melting extracts, then remove residual coal and ash and use the extracts as such or hydrogenate them in the liquid-phase to petrol, middle oil and heavy oil, or one may hydrogenate the coal in one operation to the same products and remove residual coal and ash afterwards.

Apart from the maximum possible liquefaction of coal, which is the main object of liquid-phase hydrogenation, a refining of the products is achieved simultaneously with the splitting process. Less than 20 per cent. of the oxygen and sulphur and about 50 per cent. of the nitrogen of the coal are found in the liquid final products. All the removed nitrogen and sulphur is combined with hydrogen, while the oxygen, especially in the case of brown coals, forms largely oxides of carbon. A reaction in the latter direction can be greatly favoured by hydrogenation in the presence of carbon monoxide.

The reactivity of coal is, as a rule, proportional to its content of volatile constituents. The more difficult it is to decompose the coal and the asphalts derived therefrom, the larger is usually the proportion of gaseous hydrocarbons formed (gasification). This tendency is countered by raising the hydrogen pressure and enhancing the activity of the catalyst.

In the *second stage of the reaction* hydrogenation is carried out with *fixed catalysts* over which the starting products, especially the middle and heavy oils obtained in the liquid-phase process, are passed in vapour form (*vapour-phase*), or sometimes also as liquids along with the hydrogen. Under careful control they are converted into specific improved products.

In hydrogenation with fixed catalysts the latter have a decisive influence on the result of the reaction, since they are used here in a very high concentration. The effect of the catalyst is thus much greater than in liquid-phase treatment. Many specifically acting poison-proof catalysts are now available in which the proportion of hydrogenating and splitting activity is so adjusted that it is possible to adapt the reaction to the starting material and guide it in any desired direction, while full use is made of the influences of temperature and pressure. Apart from cracking and a controlled hydrogenation, a complete refining process takes place.

The nature of the raw materials in question requires the use of poison-proof catalysts, *i.e.*, of catalysts which are insensitive to impurities known to be catalyst poisons. None of the catalysts employed is damaged by sulphur. Some catalysts show a certain sensitivity to nitrogen and oxygen compounds which can, however, be readily overcome.

The Influence of Temperature, Pressure and Re-cycle on the Reaction.

The influence of temperature is of decisive importance for the reaction. The reaction velocity of hydrogenation increases with increasing temperature, while on the other hand the equilibrium between the addition and splitting-off of hydrogen is more and more shifted towards dehydrogenation. Furthermore, the rate of splitting increases with rising temperature.

The temperature coefficient of the hydrogenation of coal in the liquid-phase, which is as a rule comparatively low (a temperature rise of 10° C. causes the reaction velocity to increase by about 50 per cent.), indicates that diffusion processes, the increased solubility of hydrogen in the oil at higher temperatures and an enhanced catalytic activity (due to desorption of substances of high molecular weight at higher temperatures) play an important part.

Olefinic double bonds are reduced at the catalyst even at 200° C., and even at room temperature. This is useful for prehydrogenations or the

hydrogenation of special products. The C—O, C—S and C—N linkages are broken and hydrogenated at temperatures of about 300° C. At still higher temperatures there is also a breaking of the C—C bonds. The refining range is thus generally found at temperatures below 400° C. while the range of cracking hydrogenation is above this temperature. The nature of the catalyst also determines the temperature to be chosen for a certain type of reactions. With some catalysts, for instance, a pronounced breaking of C—C bonds is attained even at 350° C., while with others the effects obtained at 400° are mainly refining and hydrogenation. Thus at 400° petrol is produced with little gas formation and accordingly high yield, as well as good illuminating oils and lubricating oils or asphalt-containing low-temperature carbonisation tars are hydrogenated and refined.

If the temperature is raised still further, to 450° C., middle oils are obtained from high-boiling oils and coal, while cracking is increased. At temperatures above 500° C. and at high pressures it is possible to split without hydrogenation or even to effect dehydrogenation with suitable catalysts and thus to produce knock-proof petrols with high aromatic content. This dehydrogenation naturally involves the risk of the formation of polymerisation products. Usually these dehydrogenation processes are carried out in such a way that no polymerisation products are formed. Such products may, however, be allowed to form within certain limits, and be removed before the unconverted fractions are passed again over the catalyst.

The amount of gaseous hydrocarbons will, of course, increase with rise of temperature, but this gasification can be controlled to some extent by suitable catalysts, so that the proportion of C₃ and C₄ hydrocarbons is increased at the expense of methane and ethane. Hydrogen can be saved by decreasing the formation of methane. Sometimes methane formation can be almost wholly suppressed. The C₃ and C₄ hydrocarbons are used, *e.g.*, as liquefied gases for driving engines or else they are polymerised to polymer petrol (*Polymerbenzin*). All the gaseous hydrocarbons may serve as fuel gases or for the production of hydrogen.

It should be mentioned here that the gaseous hydrocarbons formed in the liquid phase play an important part in the separation of the middle and heavy oils which are obtained from the unconverted residue by hydrogenation. The light hydrocarbons under high pressure give rise to a large increase of the vapour pressure of the middle and heavy oils, whereby much more middle and heavy oil is evaporated and carried away with the excess hydrogen than would be expected under normal pressure conditions or in the presence of hydrogen alone. Only a small fraction of this pressure increase can be accounted for by classical thermodynamics. By far the greater part is due to van der Waals' forces between the hydrocarbons. These forces cause an increase in the concentration of the heavy hydrocarbons in the highly compressed vapour of light hydrocarbons. It depends on the composition of the gaseous hydrocarbons how far this gas solubility extends and how it is shared by the different heavy hydrocarbons.

It is a quite general fact that fractionations under high pressure are very incomplete. The boiling curves of the evaporated and the residual fractions thus show a considerable overlap. The products obtained by liquid-phase hydrogenation, *viz.*, the distillate and liquid residue, are shown in Table I.

The products formed can, of course, readily be condensed by simple

cooling at such high pressures. Even normally gaseous hydrocarbons dissolve in the liquid products so that the recovery of readily vapourisable fractions of petrol is very simple. This fact renders a re-cycling of the excess hydrogen possible, because the gaseous hydrocarbons produced can only enrich the circulating gas within certain limits, and are then washed out again.

TABLE I.

Coming over up to:	Distillate.	Residue.
200°	10 %	0 %
325°	50 %	12 %
450°	97 %	55 %

Increase of hydrogen pressure usually causes more extensive hydrogenation. It can,

however, also be used for increasing the throughput without increased hydrogenation effect. At temperatures above 450° C. the hydrogen pressure in destructive hydrogenation has to be so high that the reaction does not lead to undesirable polymerisation and formation of coke. If, with suitable catalysts, the reaction can be caused to proceed without appreciable splitting, low pressures could be used with advantage, especially for the dehydrogenation of petrols. By use of high hydrogen pressures one can work at higher temperatures and with larger throughputs, without upsetting the optimum reaction conditions. The function of the highly compressed hydrogen is not necessarily merely the maintenance of the thermodynamically required equilibrium pressure. Rather, it is the increased solubility and higher diffusion velocity of hydrogen in the liquid-phase oils which constitutes an important factor greatly favouring the undisturbed course of the reaction.

As an example of the effect of pressure on the liquid-phase process we may mention the conversion of old coals or of asphalts of high molecular weight, which goes but slowly at 200 to 300 atmospheres, but proceeds without difficulty and at a satisfactory rate for large-scale production at considerably higher pressures, *e.g.*, 700 atmospheres or more. The range over which the different catalysts can be applied is, in the case of stationary catalysts, further extended by the use of *higher hydrogen pressures*. It is possible, for instance, to achieve hydrogenation with greatly reduced cracking or to obtain special effects (*e.g.*, the production of knock-proof petrols) by means of catalysts with a low hydrogenating activity. Petrol and oils prepared under such conditions may ultimately be even less rich in hydrogen than those obtained at low-hydrogen pressures.

Apart from the total pressure, the ratio of the *partial pressures of oil, vapour and hydrogen* is also of importance. The degree of hydrogenation is reduced by an increase in the partial pressure of oil vapour. By raising the partial pressure of hydrogen or lowering the partial pressure of oil vapour it is possible, on the other hand, to avoid too extensive dehydrogenation and the formation of di-olefins and polymerisation and condensation products, which might damage the catalyst by clogging it with resinous matter.

Catalytic high-pressure hydrogenation reactions, like most hydrocarbon reactions, are not completed in one run. The unconverted fractions are *re-cycled*. The heavy oil formed by liquid-phase hydrogenation, for instance, is re-cycled as pasting oil when one aims at the production of middle oils and only small amounts of petrol. If the middle oil in its turn is re-cycled while the accumulating heavy

oil is withdrawn from the process, then the yield from the hydrogenation of coal consists of heavy oil (a net gain in oil) and "liquid-phase" petrol, and, in addition, a small amount of middle oil. A raw material could be completely converted into petrol even in the liquid-phase, *viz.*, by a complete re-cycling of the middle oil. Practically no use is, however, made of this possibility, because better yields (less formation of gaseous hydrocarbons), lower consumption of hydrogen, and, on the whole, better utilisation of space and time and better refined products are obtained by dividing the process of petrol manufacture into two stages.

As a rule, not more than 50-80 per cent. of the middle oils are converted into petrol in one run even in gas-phase treatment. The unchanged middle oil is separated from the petrol by distillation and treated again. A higher yield of petrol is thus achieved with a better utilisation of the reaction chamber. Moreover, the boiling curve of the petrol can be more easily adjusted to requirements in this way.

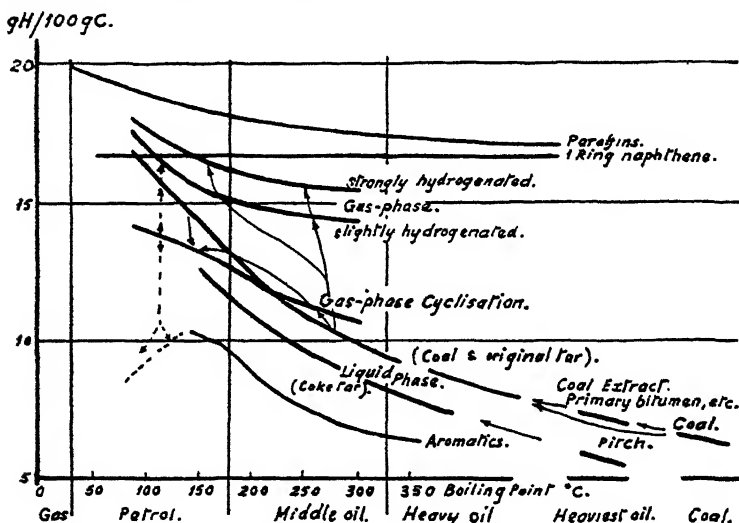


FIG. 1.—The hydrogenation of coal. (Liquid- and vapour-phase.)

—— Course of the catalytic pressure hydrogenation reaction.
 ----- Course of separation by means of solvents.

Fig. 1 represents diagrammatically the results of some dehydrogenation reactions of which the characteristic features have been described above. It shows how greatly the character of the products from the liquid-phase process is influenced by the nature of the raw material and how freely this character can be modified in the vapour-phase where stationary catalysts are used.

In the following two paragraphs this will be illustrated more fully by some examples.

The Influence of the Chemical Structure of the Raw Materials on the Properties of the Hydrogenation Products.

Middle oils which can be used as Diesel oils are obtained, for instance, when distillation residues from an asphalt base crude oil and a mixed base crude oil with a boiling-point higher than 325° C. are treated in the liquid

phase. Table II shows that the properties of these middle oils are in close agreement with the properties of the middle oils obtained from the original crude oil by distillation.

TABLE II.—MIDDLE OILS OBTAINED FROM DIFFERENT CRUDE OILS BY DISTILLATION AND LIQUID-PHASE HYDROGENATION.

Middle Oil, 180–325° C.	S.G. at 15° C.	Aniline Point, °C.	Aniline Point of Fraction.		
			210–230°.	240–270°.	280–310°.
<i>From mixed base crude oil—</i>					
Obtained by distillation . . .	0.840	61	56	59	66
By treatment in the liquid-phase	0.838	57	52	56	16
<i>From asphalt base crude oil—</i>					
Obtained by distillation . . .	0.856	50	47	50	54
By treatment in the liquid-phase	0.851	51	49	52	54

It will be seen that, in particular, the hydrogen contents of the corresponding fractions of the products obtained by distillation and from liquid-phase treatment are very similar, the hydrogen contents being characterised by the aniline point. This regularity, for which two examples are given in Table II, is found so generally that the properties of the middle oils to be obtained by hydrogenation of crude oil residues may be predicted with a high degree of accuracy if the properties of the middle oil contained in the original crude oil are known.

A similar, though less close, relation is found with coals. This is shown in Table III, where the hydrogenation middle oils from coal are compared with the corresponding middle oils from low-temperature tar. Phenols were removed from both. The agreement of the hydrogen values

TABLE III.—MIDDLE OILS OBTAINED FROM COALS BY LOW-TEMPERATURE CARBONISATION AND BY LIQUID-PHASE HYDROGENATION.

	Total Middle Oil, 180–325° per cent Phenols.	Middle Oil after Removal of Phenols (180–325° C.).			
		Density at 15° C. of the Fractions.		Aniline Point °C. of the Fractions.	
		240–270°.	280–310°.	240–270°.	280–310°.
<i>From brown coal—</i>					
Low-temperature tar	24	0.899	0.912	15	31
Liquid-phase hydro- genation . . .	14	0.878	0.906	24	33
<i>From coal—</i>					
Low-temperature tar	27	0.940	0.980	— 6	— 10
Liquid-phase hydro- genation . . .	9	0.938	0.972	— 15	— 14

is not as good as with petroleum products. This is partly due to the fact that the oils from low-temperature carbonisation represent but a comparatively small fraction of the original substance of the coal, whereas in the hydrogenation process practically the whole of the coal substance reappears in the form of oil.

Not only in liquid-phase but also in vapour-phase hydrogenation, the nature of the raw material determines the properties of the petrol obtained. The influence of the chemical structure of the starting material makes itself felt particularly in the behaviour of the petrol in engines. Table IV gives the densities and octane numbers of some petrols from

TABLE IV.—MOTOR SPIRITS FROM DIFFERENT RAW MATERIALS.

Middle Oil from:	Motor Spirit.	
	S.G.	Octane Number
Paraffin	0.680	45
Mixed-base petroleum	0.722	64
Asphalt-base petroleum	0.728	67
Shale oil paraffinic	0.712	65
Shale oil asphaltic	0.732	66
Brown-coal tar (low-temperature carbonisation)	0.734	65
Liquefaction of brown coal	0.735	66
Petroleum crack residue	0.745	74
Liquefaction of coal and extract	0.745	74
High-temperature coal tar	0.748	75

different sources prepared with comparatively active hydrogenating catalysts. The octane numbers of the petrols rise with falling hydrogen content. Motor spirits from sources of lower hydrogen content (*e.g.*, brown coal, asphalt-base petroleum, cracking residues and bituminous coal) have octane numbers of about 65 to 75. These octane numbers rise when petrols with a lower end-point are prepared.

Influence of Catalysts and Working Conditions on the Fuel Properties.

Apart from the nature of the raw materials, the catalysts and the working conditions are determining factors for the properties of the petrol in vapour-phase hydrogenation. Table V shows the extent to which the

TABLE V.—MOTOR SPIRITS FROM COAL MIDDLE OIL, PREPARED WITH DIFFERENT CATALYSTS.

Catalyst.	A.	B.	C.	D.
Density	0.735	0.745	0.770	0.830
Octane number :				
Research method	67	75	78	95
Motor method	66.5	74	75	83

quality of the petrol can be influenced by catalysts and working conditions, the raw material remaining the same. Various groups of catalysts are now available. The first and so far most important group from a technical point of view comprises catalysts (A) with a high hydrogenating and

cracking activity which can be used with all starting materials in the vapour-phase. Petrols prepared with these catalysts give octane numbers similar to those obtained from the same raw materials by low-temperature carbonisation. Column A in Table V refers to petrol prepared in this way from coal middle oil. Far better octane numbers and the same high

TABLE VI.—PETROL PREPARED WITH DIFFERENT CATALYSTS FROM MIDDLE OIL DERIVED FROM MIXED-BASE PETROLEUM.

Catalyst.	A.	B.	C.	D.
Density	0.716	0.722	0.730	0.787
Octane number :				
Research method . .	57	64	72	80
Motor method . . .	58	64	70	74

yields are secured with catalysts of the second group which exhibit a strong cracking and smaller hydrogenating activity (see columns B and C). All petrols prepared by hydrogenation with catalysts of these two groups contain comparatively large amounts of naphthenes and isoparaffins, and are characterised by their good lead susceptibility.

A third group of catalysts (D) renders possible the production of petrols

less rich in hydrogen and containing large quantities of aromatics. Here higher temperatures are used, *viz.*, about 500° C. The yield of motor spirit which was more than 90 per cent. by weight with the above-mentioned methods is now below 90 per cent. The yield is reduced when the aim is higher aromatic content or when the middle oil used is more paraffinic. Column D in Table V refers to such a petrol obtained from coal middle oil. It has an octane number of 95 (by the research method) and contains more than 50 per cent. aromatics.

The petrols obtained with catalysts of these different groups differ similarly also where middle oils from mixed-base petroleum are converted into petrol. This is shown in Table VI. A petrol with an octane number 80 (by the research method) and with more than 30 per cent. aromatics can be prepared with catalysts of group D.

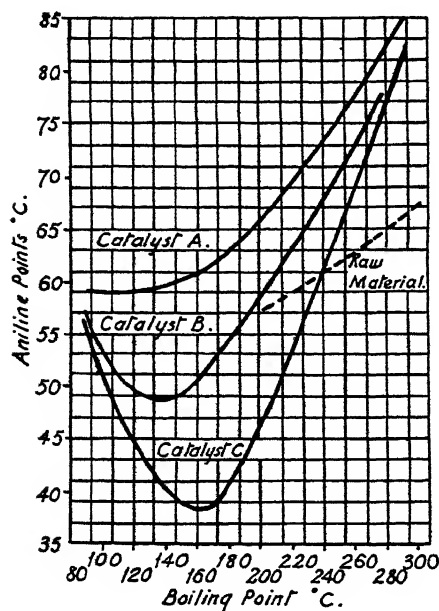


FIG. 2.—Conversion of middle oil from mixed-base petroleum into petrol. Relationship of aniline-point to boiling-point.

The differences between the petrols produced with the different catalysts are illustrated by Fig. 2, where the aniline points of the petrol and middle-oil fractions are plotted against boiling-points; the hydrogen content decreases from catalyst A to C.

Because of their stability, good anti-knock properties and satisfactory

lead susceptibility the synthetic petrols are well suited for use in aeroplane engines.

The difference in the mode of action of the various catalysts is shown also in the boiling ranges of the hydrogenation products. Fig. 3 illustrates in a qualitative and diagrammatic way the conditions encountered in the conversion of middle oil (curve 1) into petrol. Here the amounts of the different fractions are plotted against boiling temperature. Where catalysts with a high hydrogenating activity are used (A and B) the boiling range of the hydrogenation products (curve 2) is spread over a less wide range than under conditions of less powerful hydrogenation (catalyst D, curve 3). There is, therefore, less gasification with catalysts A and B (curve 2) than with catalyst D (curve 3) and the end-point of the middle oil is lower. At the same time the petrol contains a larger proportion of low-boiling fractions (below 100°) when it is prepared with catalysts A and B rather than D. This can readily be seen from Fig. 3.

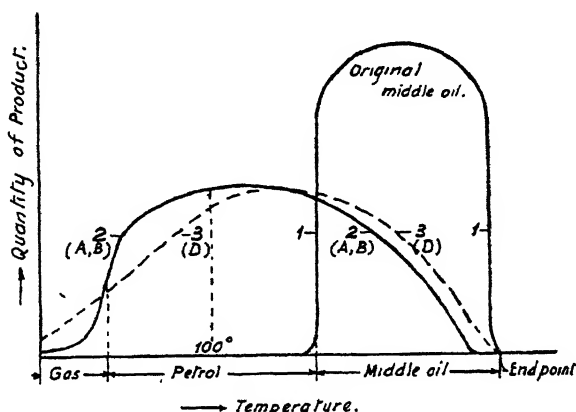


FIG. 3.—Boiling range of middle oil and hydrogenation petrols.

Fig. 3 also shows that the composition of the gaseous products depends on the catalyst used: with comparatively active hydrogenating catalysts (A and B, curve 2) substances with higher boiling-points (C_3 and C_4) are obtained in larger proportions than with catalysts of the D type (curve 3), which have a lower hydrogenating activity. Table VII shows how this influence of the different catalysts influences quantitatively the composition of the gaseous products from the hydrogenation of petroleum. The catalysts are listed in order of decreasing gasification. For reasons of comparison liquid-phase hydrogenation is also included.

TABLE VII.—COMPOSITION OF THE GASEOUS PRODUCTS FORMED DURING THE HYDROGENATION OF COAL.

Per cent by Weight.	Liquid-Phase.	Vapour-phase Catalyst.		
		D.	A.	B.
CH_4	20	18	20	2
C_2H_6	23	25	15	2
C_3H_8	35	43	45	31
C_4H_{10}	22	14	20	65
	57	57	65	96

Summary.

The chemical reactions and physical processes which take place during the high-pressure hydrogenation of coal have been described in outline. It has been shown how, by varying the catalysts and working conditions,

the manifold reactions can be controlled, thus making it possible to utilise equally well with all available raw materials, *i.e.*, coals, tars, shale oils, petroleum and their constituents, while retaining full freedom as to the choice of the final product. As well as, or instead of, high quality petrols, one may also produce Diesel oil, heating oil and from suitable raw materials also lubricating oil and paraffins in varying proportions.

With this newly acquired knowledge as to the nature and conditions of the reactions it has become possible, within the last decade, to develop a process which could keep pace with the ever-changing and ever-increasing demands upon the quality of motor fuels, and there is every reason to believe that this will continue to apply in the future.

The process can be adapted to the requirements of the finished products as well as to the raw materials available. It produces the desired mineral-oil products in highest yields from coals, tars and oils. Catalytic high-pressure hydrogenation has thus become of extraordinary importance for the maintenance of Germany's fuel supply from domestic raw materials.

GENERAL DISCUSSION.

Dr. R. Holroyd (Billingham) said: I can make only one addition to Pier's very complete summary of the reactions involved in the destructive hydrogenation of coals and lignites to give motor fuels, *viz.*, the part played by isomerisation of naphthene hydrocarbons in the vapour phase treatment of middle oils.

Probably all vapour phase catalysts, under the conditions used for hydrogenation of middle oils to petrol, favour the isomerisation of 6 carbon ring naphthenes to the corresponding methyl substituted 5 carbon ring product, for example, cyclohexane to methyl cyclopentane. Catalysis of this reaction is however, particularly marked in the case of catalysts designated B and C in tables V and VI of Dr. Pier's paper.

The reaction has an important influence on petrol quality for two reasons. Firstly, methyl substituted cyclopentanes have better anti-knock properties than the corresponding cyclohexanes. Secondly, since paraffin formation in destructive hydrogenation of aromatic middle oils results from opening the ring of an intermediate naphthene product, extensive isomerisation of the intermediate naphthenes to a more highly substituted cyclopentane product leads to the production of a more highly branched and therefore superior anti-knock paraffin.

Admittedly difference in aromatic hydrocarbon content is partly responsible for the difference in knock rating of petrols produced over catalysts A and B or C. At the same time, the higher content of cyclopentane derivatives and of branched chain paraffins in the case of B or C petrol is an important additional reason for their exceptional quality.

Dr. G. Salomon (Delft), said: Some years ago Eyring and Wynne-Jones¹ calculated from thermodynamical data that the transformation of the hexyl radical in cyclopentane should be a slow reaction with a steric factor of about 10^{-6} . There was no experimental evidence available but the results agreed with other theoretical considerations of Rice. It is therefore interesting to learn from Küchler's paper that actually no methylcyclopentane is formed during the thermal decomposition of cyclohexane. On the other hand, Nenitzescu and co-workers² effected the ring transformation with $AlCl_3$ as catalysts. It appears, therefore, that the isomerisation to 5-rings takes place at a measurable rate in solution, the actual position of the equilibrium depending on experimental conditions.

Dr. L. Küchler (Göttingen), said: In connection with the remarks of Holroyd, Hoog and Salamon I would point out that our experiments only indicate that the reaction cyclohexane \rightarrow methylcyclopentane does not

¹ *J. Chem. Physics.*, 1935, 3, 492.

² *Ber.*, 1933, 66, 1892.

occur in the *gaseous* phase. Obviously this result gives no information on the equilibrium.

Dr. H. Hoog (*Amsterdam*) said: Referring to the remarks made by the previous speaker, I would like to point out that the position of the equilibrium of methyl cyclopentane \rightleftharpoons cyclohexane is known: from the measurements of Glasebrook and Lovell³ it appears at higher temperatures *not* to be on the side of cyclohexane, but on that of methyl cyclopentane.

Prof. H. I. Waterman (*Delft*) said: On the vertical axis in Fig. 1 of Pier's paper there is shown $\text{g.H}/100 \text{ g.C}$, which factor is dependent on $\text{g.H}/100 \text{ g. (C + H)}$ or the percentage of hydrogen. Now we know that for saturated hydrocarbon mixtures this percentage of hydrogen is proportional to the specific refraction $\left(\frac{n^2 - 1}{n^2 + 2} \frac{1}{d} \right)$. On the horizontal axis in the same figure the boiling ranges are found; these are dependent on the average molecular weight of the different fractions.

It may, therefore, be expected that this diagram is appropriate for the investigation of the structure of the saturated hydrocarbon mixtures in question, *e.g.*, the number of rings. This assumption agrees with the curves indicated for the paraffins and particularly for the 1-ring naphthenes, such as cyclohexane. The last mentioned substances have indeed the formula C_nH_{2n} , which demands 16.8 g. of H per 100 g. of C, in accordance with the diagram. Therefore this diagram will also give an insight into the structure of the products obtained in the different processes, unless the fractions are afterwards carefully hydrogenated (at low temperature without changing the structure). Do the curves indeed refer to saturated fractions?

Dr. H. Fromberz (*München*), in reply to Prof. Waterman, said: As far as gas-phase products are concerned, the curves refer to saturated products.

³ Baltimore Meeting, Amer. Chem. Soc., April, 1939.

SECTION C. RING GLUCOSE AND ISOMERISATION.

A NOTE ON THE MECHANISM OF CATALYTIC DEHYDROGENATION AND CYCLISATION.

By R. C. PITKETHLY AND H. STEINER.

Received 30th March, 1939.

The application in recent years of dehydrogenation catalysts to the treatment of paraffin hydrocarbons and especially to those having chains of six or more carbon atoms, has disclosed the formation of aromatic substances through cyclisation of the paraffins.¹ Since this reaction is of great practical interest, considerable attention has been paid to its investigation. More complete accounts of these studies will probably be given in another part of the present discussion.

Although the investigations described below are incomplete it was thought possible to derive with the help of the general knowledge obtained in the study of hydrogenation reactions some conclusions as to the probable mechanism of the cyclisation reaction.

¹ Moldawski and Kamuscher, *C.R. Acad. Sci. U.R.S.S.*, 1936, 1, 355; E.P. 409,312; 466,609.

In the majority of the experiments with pure substances, the hydrocarbon studied was *n*-heptane. Treatment of *n*-heptane with a dehydrogenating catalyst at 475° C. leads to the formation of heptene and toluene. No indications of the production of cyclo-paraffins or cyclo-olefins were found nor were they to be expected since the rates of dehydrogenation of these substances to the corresponding aromatic compounds are considerably higher than those of the open-chain paraffins and olefins.² In addition, no di- and tri-olefins have been detected in the products.

Owing to the ease of dehydrogenation of hydroaromatic structures, their absence from the reaction products does not exclude their occurrence in the reaction sequence. On the other hand, it is unlikely that open-chain di- and tri-olefins should be removed so rapidly by cyclisation that no detectable amount would occur in the product. It appears, therefore, that di- and tri-olefins will play no part in the mechanism of the reaction. Cyclisation must then be effected either directly from the paraffin

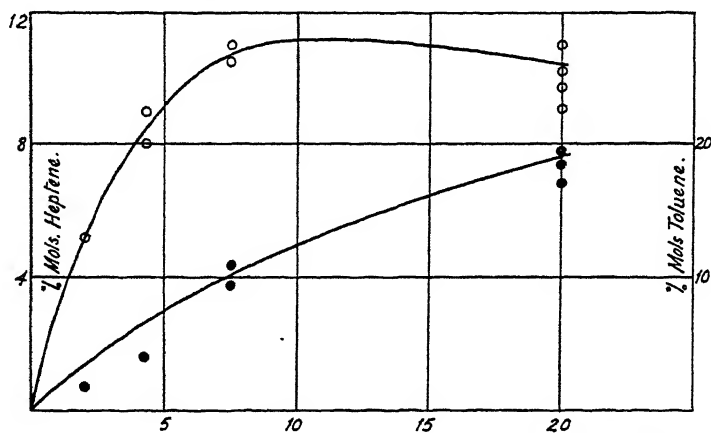


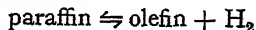
FIG. 1. Contact time in seconds.

○ Moles % heptene in liquid products.
● Moles % toluene in liquid products.

molecule or by way of the mono-olefin and the question arises whether the mono-olefin found in the product is an intermediate or a by-product of the reaction.

Experiments with varying contact time, results of which are reproduced in Fig. 1, show that except at very short contact times, the proportion of heptene in the products remains constant, while the amount of toluene formed increases steadily with increasing time of contact.

The constancy of the heptene concentration can be due either to the establishment of the equilibrium:



or simply to a stationary state in which the heptene is removed as quickly as it is formed.

In the former case, the ratio

$$\frac{[\text{H}_2][\text{C}_7\text{H}_{14}]}{[\text{C}_7\text{H}_{16}]} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

² Balandin, *Z. physik. Chem. B*, 1936, **34**, 96.

should be constant, while in the latter, assuming that heptene is formed and cyclised in unimolecular reactions, we have

$$\frac{d[C_7H_{14}]}{dt} = k_1[C_7H_{16}] = -\frac{d[C_7H_{14}]}{dt} = k_2[C_7H_{14}]$$

which leads to $\frac{[C_7H_{14}]}{[C_7H_{16}]} = \text{const.}$ (2)

That the equilibrium is not established can be seen from the experiments in which the partial pressures of hydrogen and of heptane were varied. In Table I, data of some typical experiments are given. In all

TABLE I.

Exp. No.	p_{H_2}	$p_{C_7H_{16}}$	$p_{C_7H_{14}}$	$p_{C_7H_8}$	Carrier Gas p_{N_2}	$\frac{p_{H_2} \times p_{C_7H_{14}}}{p_{C_7H_{16}}}$	$\frac{p_{C_7H_{14}}}{p_{C_7H_{16}}}$	$p_{C_7H_{14}}$ (theor.)
23	222	160	21	34	208	29	0.13	190
27	185	125	22	36	320	32	0.17	180
30	295	260	30	40	25	25	0.12	234
40	120	78	10	28	379	16	0.13	170
41	495*	99	14	25	—	67	0.14	53

All exp. at 475° C. and 20 ± 4 sec. contact time, all pressures mm. Hg.

* Exp. 41 Hydrogen used as carrier gas.

these experiments the contact time was kept constant. It is evident from the data for the partial pressures of the exit gases that the equilibrium condition (1) is not fulfilled while condition (2) is in much better agreement with the experimental facts. It was thought that at the highest partial pressure of hydrogen used (Expt. 41), the toluene might be in equilibrium with a small amount of methyl cyclohexadiene. A diminution in heptene content might then be compensated by an appreciable cyclo-olefin content with the net result that the total olefin would remain constant. However, an experiment in which pure toluene and hydrogen in the ratio 1 : 20 were passed over the catalyst at 475° C. showed that no trace of olefin was formed and this explanation must therefore be discarded.

That the paraffin-olefin equilibrium is not established in the present experiments is in agreement with thermodynamic data.³ Free energy values for 1-heptene only are available but these lead to a value of 0.07 atm. for the equilibrium constant at 475° C. of the reaction :

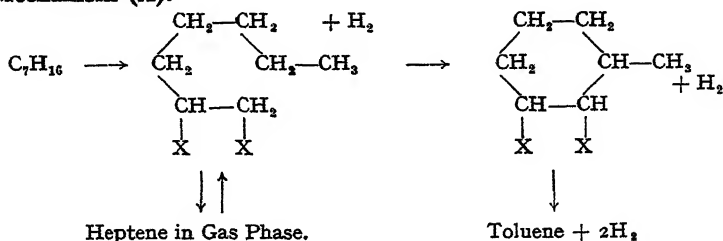


If one assumes equal probability of formation for all the isomeric *n*-heptenes (1-heptene, 2-*cis*, 2-*trans*, 3-*cis*, 3-*trans*), then one arrives at the values given in the last column of Table I for the partial pressure of mixed heptenes at equilibrium with heptene and hydrogen at the partial pressures given. Furthermore, thermodynamic data for the equilibria of isomeric *n*-butenes show that the assumption of equal probability for all the olefins is not valid and that the olefins with the double bond in the centre of the chain are formed preferentially. A similar effect in the *C*₇ series would tend to shift the equilibrium still further towards the heptenes.

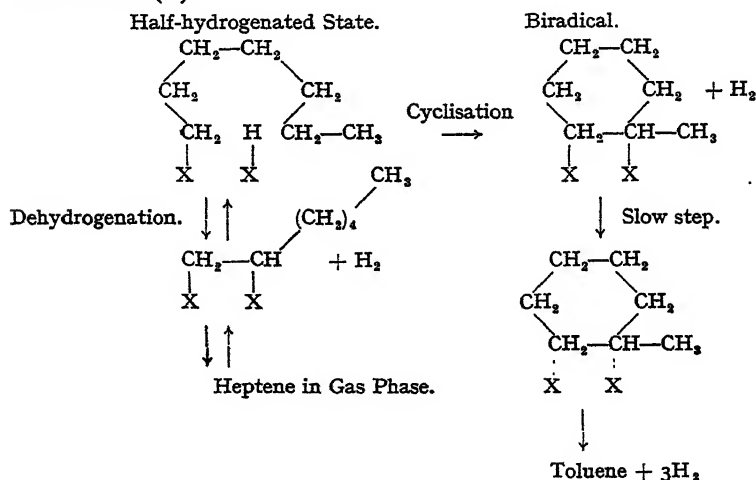
³ Thomas, Egloff and Morrell, *Ind. Eng. Chem.*, 1937, **29**, 1260.

The experimental evidence given points to the occurrence of heptene in a stationary concentration and therefore as an intermediate substance rather than as a by-product of the reaction. Using this evidence it is now proposed to discuss two different mechanisms based on some recent work on catalytic hydrogenation and on exchange reactions. These mechanisms seem plausible to us but, of course, much more experimental material will be required before any mechanism can be proved conclusively.

Mechanism (A).



Mechanism (B).



(X represents an active centre on the catalytic surface.)

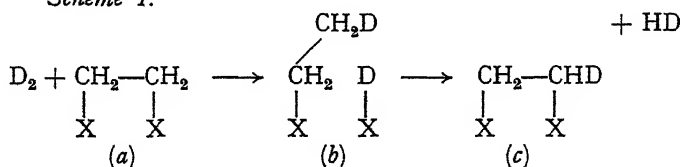
Both mechanisms assume two active centres and the orientation of the molecule on the surface is similar to the doublet configuration, as proposed by Balandin² for dehydrogenation on oxide catalysts. In the first mechanism, the adsorbed olefin is the intermediate compound and must be in equilibrium with the olefin in the gas phase. One can, of course, assume that the olefin has to be desorbed and readsorbed on another catalytic centre active for cyclisation. However, the double bond must always be considered the active part of the molecule in the adsorption process since it is known that olefins can displace paraffins and even hydrogen from catalytic surfaces.⁴ It is therefore difficult to conceive any very different orientation of the olefin on the surface than the one given in mechanism (A). The difficulty then arises that in the

⁴ A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc., A*, 1934, 146, 630.

cyclisation act only one catalytic centre is active and that the reacting carbon atom in the free chain is at a considerable distance from that centre so that any action of the catalyst due to the short-ranged exchange forces will be small.

This difficulty is overcome in mechanism (B), in which the "half-hydrogenated" state, as postulated for catalytic exchange reactions between olefins and deuterium, represents the intermediate configuration.⁵ This hypothesis has been shown to be correct for the exchange reaction between ethylene and deuterium,⁶ which proceeds according to the following scheme :

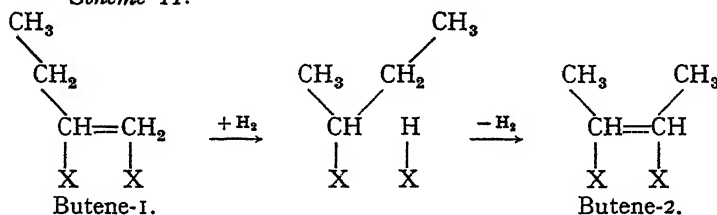
Scheme I.



Here the stage (b) represents the half-hydrogenated state and a comparison of this with the intermediate stage of mechanism (B) given above shows their close similarity. In mechanism (B), however, the "half-dehydrogenated paraffin" and not the olefin is the intermediate compound, and to comply with the experimental evidence one must therefore postulate that the "half-dehydrogenated" compound is in equilibrium with the adsorbed olefin and consequently with the olefin in the gas phase. Certain indirect evidence that this is the case is available from the experiments described in this paper.

According to the mechanism proposed, only heptane adsorbed on carbon atoms 1 or 2 is able to cyclise. It has been shown recently,⁶ however, that *in the presence of hydrogen* a very similar mechanism involving the half-hydrogenated state effects the shifting of double bonds as illustrated in scheme (II) :

Scheme II.



In the same way, heptene or heptyl radicals adsorbed on carbon atoms 3 and/or 4 could be rearranged until the points of attachment occupied the 1 and 2 positions. The rate of isomerisation by this process and consequently the rate of subsequent cyclisation should be influenced by the hydrogen concentration but, as a comparison of Expts. 40 and 41 of Table I shows, there is no such influence. Although the partial pressure of hydrogen was increased fourfold no change resulted in the final partial pressure of toluene. One must conclude, either that no shift of the

⁵ I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.

⁶ Twigg and Rideal, *Proc. Roy. Soc., A*, in the press; G. H. Twigg, *this discussion*.

double bond takes place under the conditions of the experiments or that the various olefins are in equilibrium amongst themselves, this equilibrium being independent of hydrogen pressure. At the comparatively high temperatures of the experiments (475°) the second alternative seems to be more likely. Application of scheme (II) to the intermediate stage of mechanism (B) shows that the equilibrium between the "half-hydrogenated" particle and the olefin demanded by that mechanism implies also the equilibrium between the isomeric olefins. It is hoped to clarify this point by comparing the cyclisation velocities of heptene-1 and heptene-3. The latter should either not cyclise at all if no interconversion takes place between the heptenes or it should cyclise at the same rate as heptene-1 if equilibrium of all the *n*-heptenes is established on the catalyst surface.

Mechanism B necessitates further that the half dehydrogenated molecule is in equilibrium with the biradical form, otherwise the partial pressure of the olefin in the gas-phase would depend on the square root of the hydrogen pressure which is not shown by the experiments. It seems that the rate determining step is connected with cyclisation of the biradical form which might be accompanied by partial desorption of the molecule.

There are a number of objections which might be raised to the mechanism given above. One is that the work on exchange reaction and hydrogenation which we have applied to the present problem was carried out with metallic catalysts whereas metallic oxides were used for the cyclisation experiments. However, Balandin² has shown that, at least for dehydrogenation of cycloparaffins, the results obtainable with oxide catalysts closely resemble those obtained with metals.

The second objection is that, although the "half-hydrogenated state" has been shown to occur in exchange reactions, there is, as yet, no direct evidence that it applies to hydrogenation or dehydrogenation reactions. But even if dehydrogenation is shown to occur in one stage the available experimental evidence does not exclude the "half-hydrogenated state" as an intermediate in the cyclisation act. In this case the first stage of the process would be complete dehydrogenation of the paraffin to the olefin with subsequent formation of the half-hydrogenated complex from the olefin and hydrogen.

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THE DESTRUCTIVE HYDROGENATION AND DESTRUCTION OF HEXADECANE.

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In recent years the results of the destructive hydrogenation and destruction of Rangoon paraffin wax,¹ Borneo lubricating oil fractions² and paraffinic mixtures of polymers³ have been described. In particular, the influence of the hydrogenation conditions on the changes of the cyclic character of the hydrocarbons during the experiments has been studied, using the specific refraction-molecular weight method.⁴ It was proved, *e.g.*, that the hydrocarbon molecules of Rangoon paraffin wax could be cracked without the occurrence of ring formation, when the material was heated in an atmosphere of hydrogen under high pressure, in the presence of a hydrogenation catalyst. However, when this was repeated in the absence of a hydrogenation catalyst or without hydrogen at high pressure, the reaction products contained cyclic compounds. Similar conclusions were obtained with the paraffinic mixtures of polymers.

Since so far only mixtures of hydrocarbons had been used as raw materials, the authors decided to study the destructive hydrogenation and destruction of an individual hydrocarbon of paraffinic nature. Therefore the behaviour of hexadecane was compared with the behaviour of the hydrocarbon mixtures mentioned before. In this case not only was the influence of the hydrogenation conditions on the cyclic character of the reaction products studied, but also more attention was given to the degree of branching of the products. In the latter respect conclusions could be reached partly in using the specific parachor-molecular weight method⁵ and partly by the application of the C.N.G.A.-gas distillation method.⁶

In all previous experiments nickel-on-kieselguhr had been used as a hydrogenation catalyst. In the experiments with hexadecane the influence of chromium oxide was also studied, the latter compound being well known for the preparation of cyclic hydrocarbons from paraffins at about 470° C.⁷ It is therefore of interest to compare the cyclic character of the reaction products of the destruction of hexadecane using as catalysts nickel and chromium oxide respectively.

Raw Material and Catalysts.

Hexadecane was prepared by the catalytic hydrogenation of hexadecene at 100-220° C., using high-pressure hydrogen and nickel-on-kieselguhr as catalyst.

* Experimental part carried out by G. D. A. Klijstra and H. G. Snijders.

¹ H. I. Waterman, J. J. Leendertse, L. Adam and C. van Vlodrop, *J. Inst. Petr. Techn.*, 1935, **21**, 959.

² H. I. Waterman, J. J. Leendertse and G. van der Neut, *ibid.*, 1935, **21**, 816.

³ H. I. Waterman and J. J. Leendertse, *ibid.*, 1939, **25**,

⁴ J. C. Vlugter, H. I. Waterman and H. A. van Westen, *ibid.*, 1935, **21**, 661

⁵ H. I. Waterman and J. J. Leendertse, *ibid.*, 1938, **24**, 16.

⁶ California Natural Gasoline Association tentative standard method for the analysis of natural gas by fractional distillation, *Cal. Nat. Gas. Ass. Bull.*, T.S. 321.

⁷ B. Moldavskij and H. Kamuscher, *Comptes Rendus, Acad. d. Sciences U.R.S.S.*, 1936, **1**, (X), 86.

The hexadecene was obtained by decomposing spermaceti at 360° C. and 200-300 mm. pressure.^{8, 9, 10} The product thus obtained was intensively purified. The physical constants of the final product are found in Table I, which also shows the constants of the hexadecene prepared by van Westen,^{9, 10} the author's hexadecene and van Westen's pure hexadecane.^{9, 10}

From the physical constants described in literature for *n*-hexadecane¹¹ it can be concluded that hexadecane previously so prepared can be considered to be a normal product.

The nickel-on-kieselguhr catalyst was the ordinary preparation always used in our hydrogenation experiments. It was prepared by precipitation of nickel hydroxide on kieselguhr (by neutralisation of a nickel sulphate solution) followed by reduction of the nickel hydroxide under atmospheric pressure at 500-550° C.

The chromium oxide was prepared by thermal decomposition of ammonium bichromate, followed by an intensive washing of the resultant compound with distilled water, drying and reduction under atmospheric pressure at 400-430° C. It was proved that the chromium oxide thus obtained was a suitable catalyst in the preparation of toluene from *n*-heptane.

TABLE I.

Physical Constants.	Hexadecene.	Hexadecene, van Westen.	Hexadecane.	Hexadecane, van Westen.
n_D^{20}	1.4414	1.4419	1.4350	1.4352
d_4^{20}	0.7821	0.7825	0.7748	0.7751
Specific refraction (r_D^{20})	—	—	0.3368	0.3368
Surface tension (σ_{20})	—	—	27.92	—
Specific parachor (p_{20})	—	—	2.967	—
Number of rings per molecule				
from r_D^{20}	—	—	0.1	0.1
from p_{20}	—	—	0	—
Molecular weight (cryoscopic- ally in C_6H_6)	—	—	230	—
Solidifying-point (°C.)	3.4°	2.2°	14.8°	17.8°
Bromine value (McIlhenny)	68	71.2	0	—

Description of the Experiments.

All experiments were made in a 2 l. rotating autoclave under standard conditions. 250 g. of hexadecane were always heated for one hour at the reaction temperature in the presence of high-pressure hydrogen or nitrogen (initial pressure at room temperature 80 kg./cm.²) and 10 per cent. (by weight) of catalyst.

The experiments were quantitative, the amounts of gaseous and liquid products being determined as accurately as possible and always in the same way. By cooling in liquid air the reaction gases from the autoclave were separated into a low-boiling and a higher-boiling part. The volume of both gas fractions was measured at room temperature and each fraction was analysed in the ordinary way using mercury as a sealing-liquid. The mean number of carbon atoms per molecule in the paraffinic part of the

⁸ F. Kraft, *Ber.*, 1883, 16, 3018.

⁹ H. A. van Westen, *Thesis Delft*, 1931.

¹⁰ H. I. Waterman, P. van't Spijker and H. A. van Westen, *Rec. Trav. Chim.*, 1929, 48, 1103.

¹¹ Compare A. V. Grosse and G. Egloff, *Physical Constants of Paraffin Hydrocarbons*, U.O.P. booklet 219, Universal Oil Products Co., Chicago, Ill.

gases was determined by combustion of the paraffins over CuO at about 860°, followed by a determination of the quantity of carbon dioxide thus formed. Sometimes the gases were analysed also by means of a C.N.G.A. distillation.⁶

The liquid products of all experiments were fractionated quantitatively under standard conditions (partly under vacuum, in order to avoid high temperatures during the distillation). The fractions were analysed by the specific refraction method⁴ and partly by the specific parachor method.⁵ Thus the number of rings per molecule in each fraction could be deduced, whereas the number of rings found from the specific parachor less the number of rings from the specific refraction gave an idea of the degree of branching of the reaction products.

Sometimes the products of the reaction were unsaturated, in these cases a careful non-destructive hydrogenation of the fractions was necessary for the analysis.

In the analysis by means of the methods mentioned before, the refractive index was determined with the Abbe refractometer, the molecular weight was measured cryoscopically in benzene. For the determination of the surface tension sometimes the stalagmometric method was used,¹² another time the ring-method (apparatus of Cenco- du Noüy.¹³ In other cases both methods were applied.

Results.

Five experiments were carried out (indicated by the Figs. 1, 2, 3, 4, and 5). In experiments 1, 2, and 3 the hexadecane was submitted to a destructive hydrogenation, in 1 the reaction temperature being 450° C., in 2 and 3, 435° C. (430-440° C.). At 450° C. a very marked destruction was observed; the reaction gases contained as yet no hydrogen. So during a part of the reaction time the hydrocarbons were heated at 450° under cracking conditions without an excess of hydrogen, and consequently the experiment was not merely "a destructive hydrogenation." In this respect better results were obtained at 435° C., so all other experiments were carried out at this temperature.

In Table II the physical constants of all fractions are summarised, as well as the yield of the reaction products is given (calculated in percentages by weight of the raw material). Table III gives a more complete survey of the composition of the gaseous reaction products. The numbers of rings per molecule deduced from the specific refraction as well as from the specific parachor has been indicated in Table IV. The number of ("extra") branches in the products equals ten times the difference in the number of rings from the specific parachor and from the specific refraction.

The reaction products of the "destructive hydrogenation" experiments 2 and 3 were practically completely saturated; in the other experiments, which were carried out under cracking conditions, the liquid fractions contained unsaturated compounds.*

In all experiments the greatest part of the raw material had been converted into lower-boiling hydrocarbons. Particularly in the case of the nickel experiments 1, 2, and 4 an important quantity of gaseous hydrocarbons was formed.

On considering the yields of the reaction products of experiments 2-5, special attention may be given to the differences in the quantity of the fractions with a molecular weight higher than the molecular weight of the

¹² Compare J. J. Leendertse, *Thesis Delft*, 1938.

¹³ D. J. W. Kreulen, *J. Inst. Petr. Techn.*, 1938, **24**, 554.

* This conclusion was deduced by comparison of the aniline points observed and the aniline points read from a diagram, as yet not published. The latter graph is similar to the specific refraction-molecular weight-aniline point diagram for saturated hydrocarbon mixtures communicated before,⁴ but it comprises the molecular weight range of 140-250.

TABLE II.

Physical Constants.	Fraction Number.							
	Gases.	I.	II.	III.	IV.	V.	VI.	VII.
*1. Hydrogen and Nickel, 450° C., 1 hour.								
Yield per cent. . .	38.8	8.9	10.7	13.6	9.2	15.6	3.3	—
n_D^{20}	—	1.3600	1.3882	1.4122	1.4283	1.4382	1.4615	—
	—	—	1.3829	1.4054	1.4220	1.4341	1.4582	—
$d_{40}^{20}/4$	—	0.6275	0.6859	0.7267	0.7591	0.7782	0.8166	—
	—	—	0.6760	0.7204	0.7530	0.7745	0.8111	—
Specific refraction (r_D^{20})	—	0.3517	0.3442	0.3425	0.3391	0.3375	0.3363	—
	—	—	0.3450	0.3405	0.3375	0.3363	0.3365	—
Mean molecular weight	—	81	90	123	163	217	268	—
	—	—	92	123	160	215	258	—
Aniline point (° C.) .	—	—	59.3	60.3	67.9	84.5	83.8	—
	—	—	67.5	70.4	77.6	89.3	84.5	—
	—	—	—	—	—	—	101	—
Bromine value . . .	—	32	29	19	13	6	2	—
	—	—	—	0	0	0	—	—
*2. Hydrogen and Nickel, 435° C., 1 hour.								
Yield per cent. . .	37.2	6.1	7.6	13.5	10.3	8.2	14.8	2.2
n_D^{20}	—	1.3510	1.3838	1.4053	1.4207	1.4285	1.4340	1.4385
$d_{40}^{20}/4$	—	—	0.6741	0.7178	0.7462	0.7616	0.7720	0.7812
Specific refraction (r_D^{20})	—	—	0.3467	0.3417	0.3396	0.3382	0.3373	0.3364
Surface tension (20° C., dynes/cm.)	—	—	—	22.39	25.18	26.55	27.62	—
Specific parachor (p_{20})	—	—	—	3.030	3.002	2.981	2.970	—
Mean molecular weight	—	—	94	129	168	199	227	245
Aniline point (°C.) .	—	—	67.0	70.4	80.2	86.8	93.2	95.1
	—	—	—	—	—	—	(96)	99
Bromine value . . .	—	—	—	—	—	0	0	0
*3. Hydrogen and Chromium Oxide, 435° C., 1 hour.								
Yield per cent. . .	3.8	3.8	4.7	8.9	7.5	10.3	60.2	0.8
n_D^{20}	—	1.3580	1.3810	1.4050	1.4207	1.4310	1.4349	1.4420
$d_{40}^{20}/4$	—	—	0.6688	0.7159	0.7469	0.7661	0.7740	—
Specific refraction (r_D^{20})	—	—	0.3472	0.3424	0.3393	0.3379	0.3371	—
Surface tension (20° C., dynes/cm.)	—	—	—	22.52	25.22	26.92	27.56	—
Specific parachor (p_{20})	—	—	—	3.043	3.000	2.973	2.960	—
Mean molecular weight	—	—	91	128	169	206	233	—
Aniline point (° C.) .	—	—	—	73.9	82.0	90.3	94.7	—
	—	—	—	—	—	—	(97)	—
Bromine value . . .	—	—	—	0	3	1	0	—

* Experiments 1, 2, and 3 were carried out by G. Klijnstra and Nos. 4 and 5 by H. G. Snijders. The physical constants *after* hydrogenation are shown in italics; the aniline point read from the

TABLE II. (continued).

Physical Constants.	Fraction Number.							
	Gases.	I.	II.	III.	IV.	V.	VI.	VII.
* 4. Nitrogen and Nickel, 435° C., 1 hour.								
Yield per cent. . . .	13.4	4.0	11.8	11.7	19.2	7.3	19.3	13.3
n_D^{20}	—	1.367 (0°)	1.388 (0°)	1.4123 1.4091	1.4351 1.4253	1.4440 1.4360	1.4442 1.4388	1.4666 1.4542
$d_{40}^{20}/4$	—	0.623 (0°)	0.678 (0°)	0.7297 0.7293	0.7748 0.7619	0.7899 0.7825	0.7913 0.7853	0.8299 0.8173
Specific refraction (r_D^{20})	—	—	—	0.3412 0.3391	0.3368 0.3358	0.3363 0.3341	0.3358 0.3347	0.3341 0.3314
Surface tension (20° C., dyne/cm.)	—	—	18.8	22.56 22.56	24.89 24.89	26.82 26.82	27.62 27.62	28.78 28.78
Specific parachor (p_{20})	—	—	—	2.988 2.988	2.932 2.932	2.908 2.908	2.919 2.919	2.834 2.834
Mean molecular weight	—	70	82 81	105 112	144 146	185 193	216 215	255 268
Aniline point (° C.) .	—	—	—	49.5 65.9	60.1 73.6	73.6 82.9	86.9 91.6	84.0 94.4
	—	—	—	—	—	—	—	96
Bromine value . . .	—	58	55 0	43 0	33 0	16 0	11 0	10 0
* 5. Nitrogen and Chromium Oxide, 435° C., 1 hour.								
Yield per cent. . . .	6.4	4.0	11.4	20.3	10.9	8.2	13.7	25.2
n_D^{20}	—	1.375 (0°)	1.389 (0°)	1.4124 1.4048	1.4322 1.4250	1.4403 1.4344	1.4431 1.4386	1.4550 1.4494
$d_{40}^{20}/4$	—	0.627 (0°)	0.671 (0°)	0.7300 0.7233	0.7700 0.7631	0.7862 0.7804	0.7908 0.7864	0.8124 0.8078
Specific refraction (r_D^{20})	—	—	—	0.3411 0.3387	0.3370 0.3351	0.3354 0.3340	0.3353 0.3342	0.3340 0.3322
Surface tension (20° C., dyne/cm.)	—	—	19.0	22.78 3.020	25.36 2.941	26.37 2.904	27.53 2.913	28.63 2.863
Specific parachor (p_{20})	—	—	—	—	—	—	—	—
Mean molecular weight	—	73	82 79	108 110	143 146	175 176	202 204	261 263
Aniline point (° C.) .	—	—	—	52.7 65.5	62.3 72.9	72.5 81.0	83.2 88.5	89.2 94.6
	—	—	—	—	—	—	—	97
Bromine value . . .	—	69	47 0	40 0	29 0	22 0	13 0	10 0

TABLE III.

Experiment with—	Yield Per Cent. (by Weight) of Gases on Raw Material.	Analysis of the Saturated Part of the Hydrocarbons in the Gases. (Yields in Per Cent. by Weight on the Total Raw Material of the Experiment.)	Unsaturated Hydrocarbons in the Gases.
Hydrogen and nickel, 450° C., 1 hour (1)	38.8	37.0 per cent. containing a mean number of C-atoms per molecule of 1.4. 1.8 per cent. containing a mean number of C-atoms per molecule of 2.9.	Only traces
Hydrogen and nickel, 435° C., 1 hour (2)	37.2	31.7 per cent. containing 18.2 per cent. CH ₄ , 5.6 per cent. C ₂ H ₆ , 6.7 per cent. C ₃ H ₈ , and 1.2 per cent. <i>n</i> . C ₄ H ₁₀ . 5.5 per cent. containing a mean number of C-atoms per molecule of 2.9.	
Hydrogen and chromium oxide, 435° C., 1 hour (3)	3.8	2.1 per cent. containing a mean number of C-atoms per molecule of 1.0. 1.7 per cent. containing a mean number of C-atoms per molecule of 2.4.	
Nitrogen and nickel, 435° C., 1 hour (4)	13.4	Containing 10.0 per cent. CH ₄ , 1.3 per cent. C ₂ H ₆ , 1.6 per cent. C ₃ H ₈ , and 0.5 per cent. <i>n</i> . C ₄ H ₁₀ .	Maximal a few per cents.
Nitrogen and chromium oxide, 435° C., 1 hour (5)	6.4	1.2 per cent. containing a mean number of C-atoms per molecule of 1.0. 5.2 per cent. containing a mean number of C-atoms per molecule of 2.0.	

raw material. In the destructive hydrogenation experiments 2 and 3 the quantity of latter fractions was negligibly small, contrary to the cracking experiments 4 and 5. The latter difference points, already, to a different course of the reactions in both groups of experiments. The presence of products with a molecular weight higher than that of the raw material can only be explained by polymerisation (or condensation) of unsaturated hydrocarbons. Therefore it must be caused by side reactions of the cracking products of hexadecane. In the destructive hydrogenation experiments the polymerisation reaction evidently has not occurred at all or only to a much smaller extent, the quantity of high-molecular products being negligibly small in the experiments 2 and 3. Similar differences between the destructive hydrogenation and cracking experiments may be expected also for the occurrence of other side reactions, such as cyclisation.

The latter conclusions are supported by the results of the determination of the cyclic character and the degree of branching of the reaction products. If secondary reactions had been practically absent in the destructive hydrogenation experiments, it might be expected that the resultant reaction products should be normal paraffins, whereas in the case of the cracking experiments cyclic and branched products might be formed. The specific refraction of the products of experiments 2 and 3 indicates a completely paraffinic character of the liquid fractions, indeed.* The number of rings derived from the specific parachor is 0 in most cases, whereas the difference in the number of rings from the specific parachor and the specific refraction

* In most cases even a small negative number of rings per molecule was observed (— 0.1). A similar deviation was found also for several other normal hydrocarbons and may indicate a *small* inexactness in the atomic refraction values of Eisenlohr, on which the specific refraction graph is based. Kreulen^{12a} observed similar differences for other paraffinic products.

nearly never exceeds the value 0.1. Therefore these analyses give no indication of the formation of cyclic or branched hydrocarbons during the experiments. The results of the C.N.G.A. gas distillation of the gases and the lowest boiling liquid fraction from experiment 2 supported this conclusion. These products contained butane, *viz.* *n*-butane.

Also in the case of the cracking experiments the nature of the reaction products came up to expectation. The liquid fractions were partly cyclic in nature (compare also Table IV). The differences in the number of rings deduced from the specific parachor and the specific refraction increased in comparison with the corresponding differences in the destructive hydrogenation experiments, in the case of the relatively high molecular fractions.† No special cyclisating action of the chromium oxide was observed under these conditions.

All the results can be explained completely in the following way. Under the conditions described before, the hexadecane molecules must be cracked or dehydrogenated first. The unsaturated hydrocarbon residues thus primarily

† Similar results were obtained for three fractions of the Bergin-

sation experiments with Rangoon paraffinic wax,¹ of which had been proved before that they contained cyclic compounds.

TABLE IV.

Fraction Number.	Molecular Weight.	Number of Rings Per Molecule		Difference 2 - 1.
		from r_D^{20} (1).	from p_{20} (2).	
1. Experiment with Nickel and Hydrogen, 450° C.				
I	—	—		
II	92	0.1		
III	123	0.1		
IV	160	0.2		
V	215	0		
VI	258	- 0.2		
VII	—	—		
2. Experiment with Nickel and Hydrogen, 435° C.				
I	—	—	—	—
II	94	- 0.1	—	—
III	129	0	0.1	0.1
IV	168	- 0.1	0	0.1
V	199	- 0.1	0	0.1
VI	227	- 0.1	- 0.1	0
VII	245	- 0.1	—	—
3. Experiment with Chromium Oxide and Hydrogen, 435° C.				
I	—	—	—	—
II	91	0	—	—
III	128	- 0.1	0	0.1
IV	169	- 0.1	0	0.1
V	206	- 0.1	0	0.1
VI	233	- 0.2	0	0.2
VII	—	—	—	—
4. Experiment with Nickel and Nitrogen, 435° C.				
I	—	—	—	—
II	—	—	—	—
III	112	0.3	0.4	0.1
IV	146	0.4	0.5	0.1
V	193	0.4	0.6	0.2
VI	215	0.3	0.4	0.1
VII	268	0.6	1.1	0.5
5. Experiment with Chromium Oxide and Nitrogen, 435° C.				
I	—	—	—	—
II	—	—	—	—
III	110	0.3	0.2	- 0.1
IV	146	0.5	0.5	0
V	176	0.5	0.6	0.1
VI	204	0.3	0.5	0.2
VII	263	0.5	0.8	0.3

formed may react in several ways. In the presence of nickel or chromium oxide and high-pressure hydrogen they may be hydrogenated immediately, forming saturated hydrocarbons. The latter compounds can be cracked again, the parts hydrogenated, etc. However if the hydrogenation conditions are less favourable, or if the hydrogenation velocity is smaller than the reaction velocity of other possible reactions of the unsaturated hydrocarbon residues, other reactions may occur, *e.g.*, cyclisation, polymerisation and condensation. The results obtained in the destructive hydrogenation experiments point to a very rapid hydrogenation of the primary destruction products. However the results of the cracking experiments indicate clearly secondary reactions of the unsaturated cracking products.*

In most experiments the yield of methane is relatively high in comparison with each of the other gaseous hydrocarbons (mostly about the half or more is methane), though it is always small in comparison with the total yield of products with a molecular weight lower than the molecular weight of the raw material. Particularly in the case of the hydrogenation experiments 2 and 3 the cracking of the hydrocarbon molecules can have occurred only partly in the final C—C bonds; the molecules must have been broken for an important part at other C—C bonds, if the supposition is made that primarily formed methane (or methyl- and methylene radicals) have not been converted into higher molecular products.

Summary.

The destructive hydrogenation and cracking of hexadecane at 435° C. (time of heating one hour) has been studied quantitatively using nickel-on-kieselguhr and chromium oxide as catalysts.

The result of the destructive hydrogenations of hexadecane was a series of normal (or practically normal) paraffins with a molecular weight lower than the molecular weight of the raw material, indicating a very rapid hydrogenation of the primary destruction products, in such a way that other reactions could practically not occur. However in the case of the cracking experiments the reaction products were partly of cyclic and branched nature. This points to secondary reactions of primary unsaturated destruction products. Cyclisation as well as polymerisation (or condensation) reactions have occurred.

From the yield of methane in the destructive hydrogenation experiments in comparison with the yield of the other destruction products in these experiments could be deduced that the destruction of the hydrocarbon molecules can have occurred only partly at the final C—C bonds of the molecules, if the supposition is made that primarily formed methane (or methyl- and methylene radicals) have not been converted into higher molecular compounds.

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* In comparing for experiments 2, 3 and 5, the yield of gaseous products and of hydrocarbons with a molecular weight corresponding with the molecular weight of the raw material hexadecane, one might suppose a difference in the primary destructive action of the nickel catalyst and the chromium oxide. In the nickel experiments the primary reaction might have been a rupture of C—C bonds which will not be influenced very much by the presence of high pressure hydrogen. In the case of the chromium oxide experiments the first reaction might have been a dehydrogenation of the hexadecane, which will be suppressed to a large extent by the high-pressure hydrogen (compare experiment 3). However, the authors believe that this conclusion cannot be drawn without further enlargement of the number of experiments.

INVESTIGATIONS INTO THE CYCLISATION (AROMATISATION) OF ALIPHATIC HYDROCARBONS.

By H. HOOG, J. VERHEUS AND F. J. ZUIDERWEG.

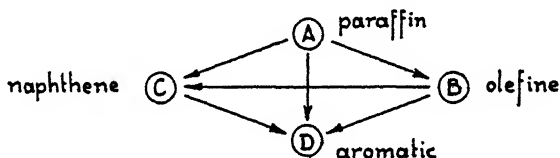
Received 24th February, 1939.

In some recent publications^{1,2,3,4,5,6} reactions are described by which paraffins are catalytically converted to aromatics without marked cracking or polymerisation.

From a technical point of view the realisation of such reactions would be very important, aromatics having a considerably higher anti-knock value than the corresponding unbranched, or slightly branched aliphatic hydrocarbons. Furthermore, aromatisation of aliphatics might also be of importance for the production of certain aromatics for the chemical industry.

The Russian publications quoted ^{1,2} go to show that, from a scientific point of view, several interesting problems are attached to this reaction.

The conversion from paraffin to aromatic may be conceived to take place in various ways, as shown in the following diagram :



From a thermodynamic point of view, any of these ways would seem possible ; along AB, AC and BC we are concerned with equilibria which occupy a central position (the equilibrium constants, K_p , being of the order of magnitude of $10\text{-}10^2$, $10\text{-}10^2$ and $1\text{-}5$ respectively) at the cyclisation temperatures used in ^{1,2} the investigations mentioned above (Cr_2O_3 catalyst : $450\text{-}500^\circ\text{C}$.), whereas along AD, BD and CD the equilibria are entirely on the side of the aromatic (K_p = about 10^{-5}).

What actually happens depends on the reaction velocities along the possible paths, such velocities being strongly influenced by the catalysts used.

The study of these reaction velocities is of great importance ; they not only govern the selection of the base materials to be used (whether paraffins, or non-paraffinic hydrocarbons), but they also determine whether the cyclisation reaction might be directed under such conditions that naphthenes are formed instead of aromatics.

¹ B. L. Moldawski and G. D. Kamuscher, *C.R. Ac. Sci. U.S.S.R.*, 1936, 1, (X), 355.

² B. L. Moldawski, G. D. Kamuscher and M. V. Kobylskaya, *J. Gen. Chem., U.S.S.R.*, 1937, 7, 169.

³ B. Moldawski, G. Kamuscher and M. Kobylskaya, *ibid.*, 1835.

⁴ B. Moldawski, F. Bezprozvannaya, G. Kamuscher and M. Kobylskaya, *ibid.*, 1840.

⁵ B. A. Kazansky and A. F. Plate, *Ber.*, 1936, 69, 1862.

⁶ A. V. Grosse, J. C. Morrell and W. Mattox, *Div. of org. chem. Amer. Chem Soc.*, Meeting at Milwaukee, September, 1938.

As we found from some tentative experiments carried out in connection with the first-mentioned publication¹ that Cr_2O_3 is really an effective catalyst for the conversion of aliphatics to aromatics, we made numerous experiments in order to discover the extent to which various types of hydrocarbons could be aromatised and, at the same time, to acquire a better understanding of the mechanism of the reaction.

To this end we ascertained for a number of different hydrocarbon types with varying numbers of carbon atoms and of varying structure* the extent to which the reaction(s) take(s) place under a given set of reaction conditions, and determined the constitution of the individual products which had been formed.

In order to complete the picture of the reaction mechanism obtained in this investigation, we are now carrying out some reaction-kinetic measurements for which only two hydrocarbons from the above-mentioned series are being used, *viz.*, *n*-heptane and *n*-heptene.

As this further investigation has not yet been completed, we shall only mention some preliminary results in this paper.

Comparative Cyclisation of Various Base Materials ; Identification of the Products Formed.

I. Catalysts and Experimental Conditions Applied.

As catalytic material a specially prepared pilld Cr_2O_3 was used. A charge of these pills was slowly heated up to the working temperature ($465^\circ\text{C}.$) in a current of hydrogen over a period of two hours, whereupon the hydrocarbon under test (in the gaseous state) was passed over the catalyst.

Fig. 1 illustrates the equipment employed. As to the condensation system used, it should be noted that as the receivers connected to the condensers were kept at room temperature, only a very small amount of dissolved gases remained behind in the condensates; on the other hand, owing to the use of the solid CO_2 -cooler, only very few liquid reaction products were left in the gas stream. The non-condensed gases were measured and then analysed.

The test conditions used in all experiments were :

Catalyst										
Volume in ml.	about 40
Weight in g.	" 55
In each experiment a fresh catalyst charge was used.										
Duration in hours.	about 5
Temperature, $^\circ\text{C}.$	465
Base material feed ml./h.	17.5
Flow rate g./g. of cat./h.	about 0.22
Contact time, sec.	18-24
Space velocity per min.	$2\frac{1}{2}$ -3 $\frac{1}{2}$

Under these conditions moderate quantities of hydrocarbons were converted, the procedure giving satisfactory check values, as may be illustrated by the results of two experiments carried out with *n*-octane as the base stock :

* The preparation and properties of most of these hydrocarbons are described in *Rec. Trav. Chim.*, 1939, 58, 329, by J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff and J. Smittenberg.

Base material	n-octane	
Experiment No.	57	58
Catalyst No.	C ₁₆	C ₁₆ *
Generation of gas per cent. by weight on intake	7	8
Gas analysis :		
vol. per cent. H ₂	95.0	92.0
" C _n H _m	0.2	0.5
" C _n H _{2n+2}	4.8	6.2
Liquid reaction product :		
per cent. by weight on intake	84	84
Aromatics, per cent. by weight	49	51
Naphthenes, " "	0	0
Olefines, " "	11	10
Paraffins, " "	40	39

* Fresh catalyst from same batch.

In all cases only a comparatively slight decline in activity took place while the experiments were proceeding (as shown by the gas production), so the results were not affected by appreciable differences in average cata-

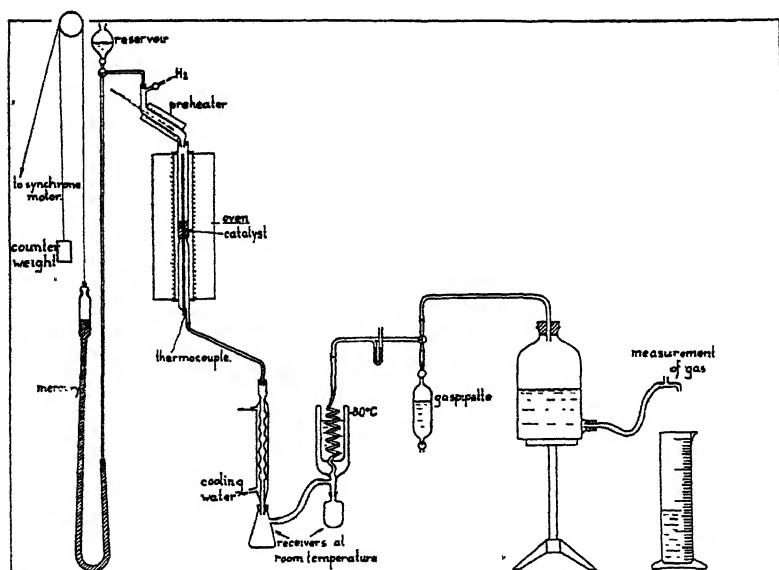


FIG. 1.—Equipment for cyclisation experiments.

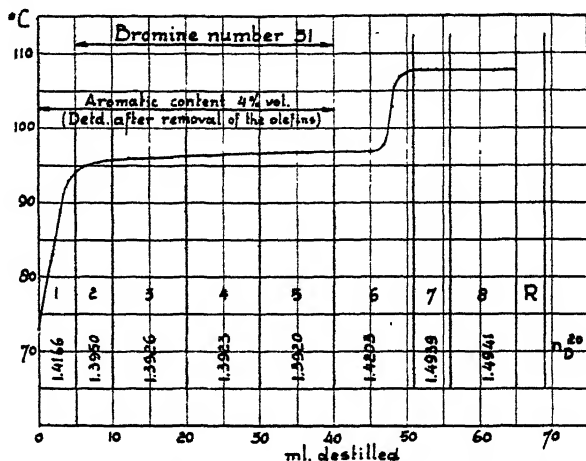
lytic activity. With the naphthenes investigated, however, the catalyst needed a considerable period to attain its full activity; if their conversion had been determined with a catalyst at its maximum activity, the figures would have been about one-third higher than those given below.

II. Analytical Methods.

Gas Analysis.—The non-condensed reaction gases were analysed by the Bunte-Jaeger method. All the gases examined were very rich in hydrogen; they contained practically no olefines at all and invariably a small quantity of paraffin hydrocarbons. In some cases we made a more detailed investigation, in order to establish the nature of these paraffin hydrocarbons; for this purpose we used a method developed by Scheffer and Mulders⁷ by which the CH_4 content can be determined apart from the content of higher paraffins; 60-70 per cent. of the paraffins present in the reaction gases were found to consist of methane.

Analysis of the Liquid Reaction Products.—The results of a very sharp fractionation (using a column equivalent to about twenty-two theoretical plates, operating hold-up 15 ml.) gave a provisional idea of the composition of the reaction product. The refractive indices and the bromine numbers of the fractions thus obtained enabled us to estimate their content of aromatics and olefines. In Fig. 2 a rectification curve of a reaction product of *n*-heptane is given.

FIG. 2.—Rectification curve of a cyclisation product of *n*-heptane. Intake 70 ml. Dist. 65 ml. Residue 4 ml. Loss 1 ml.



A subsequent portion of the reaction product was examined as follows:

The total quantity of *olefines* present was calculated on the basis of the bromine value and the (estimated) molecular weight, assuming only aliphatic mono-olefines to be present.

After removal of the olefines with thio-glycolic acid (reaction taking place at room temperature in a homogeneous propionic acid solution, a reaction time of about sixteen hours being invariably applied; this method has been described by Hoog and Eichwald in *Rec. Trav. Chim.*, 1939, 58, 481), the total quantity of *aromatics* was determined by treating the product with 98 per cent. sulphuric acid (fifteen minutes' shaking with three volumes of H_2SO_4).

In some cases the olefines were also removed by means of selective hydrogenation, after which the aromatic content was again determined by sulphonation. The results of both methods of aromatic determination tallied closely.

Finally, the *naphthene* content was ascertained by determining the aniline point of the olefine-free and aromatic-free product.

In addition to determining the principal groups of components quantitatively, we isolated and identified a number of the more important individual compounds present in the cyclisation products.

⁷ *Rec. Trav. Ch.*, 1930, 49, 1057.

Olefines.—As it was found impossible to isolate the olefines direct by rectification, we used a method developed by Brame and Hunter,⁸ which is based on bromination of the hydrocarbon-mixture, isolation of the di-bromide by distilling off the unconverted hydrocarbons under suitable conditions and, finally, conversion of the dibromide to olefine with the aid of zinc dust. The crude isolated olefines were purified by rectification in a small rectification column (about seven theoretical plates, operating hold-up about 1 ml.) and identified on the basis of their physical constants.

Aromatics.—The principal aromatic product could almost invariably be isolated by rectification; in some cases (*viz.* where benzene, toluene or para-xylene proved to be the main component), identification was possible on the basis of physical constants (for reference material see U.O.P. Booklet 217); in other cases we made use of:

- (1) A method developed by Moldavski and others,² consisting in oxidation of the aromatics to aromatic acids, separation of the acids formed and identification of these;
- (2) A nitration procedure worked out by Reichel;⁹ and
- (3) Bromination as mentioned by Meyer.¹⁰

III. Results Obtained in the Comparative Experiments with Various Hydrocarbons in the Presence of Cr_2O_3 Catalyst.

A fairly large quantity of catalyst was prepared at a time; however, for practical reasons this procedure had to be repeated several times in the course of our investigation.

The catalysts used in the various experiments have in consequence been taken from different batches; as appeared from comparative experiments made with *n*-octane and with *n*-heptane as base material, the results obtained with different catalysts generally varied comparatively little. By considering the aromatic contents found in the reaction products of *n*-octane as a measure for the "activity per unit volume of catalyst," we calculated a conversion factor by means of which all quantitative results obtained could be approximately converted to the values which would have been found if a catalyst had been used, possessing a "standard catalyst activity."

The agreement between the converted values for a given hydrocarbon over different catalysts was generally satisfactory and of the same order of magnitude as the agreement between the results of duplicate experiments with one and the same catalyst.

In one case, however, we felt that this method should not be applied; the catalyst used for the experiments with heptene-1 and heptene-2 proved to be very active; consequently, if the results had been converted as indicated above, rather radical corrections would have had to be made which we did not consider justified. We therefore give the results of the *n*-heptene experiments with the catalyst used, without conversion to standard catalyst activity.

All data of a quantitative nature obtained in our comparative experiments, corrected for differences in catalyst activity, have been summarised in Table I which shows in column:

- (1) The name of the hydrocarbon concerned.
- (2) The yield of liquid reaction product calculated as a percentage by weight of the base material.
- (3) A figure, the difference between which and 100 denotes to what extent splitting and/or synthetic reactions have taken place. This figure was derived from rectification data of the reaction products.

⁸ J.I.P.T., 1927, 13, 794.

⁹ H. P. Reichel, *Chem. Z.*, 1931, 55, 744.

¹⁰ Hans Meyer, *Nachweis und Bestimmung Organischer Verbindungen*, Berlin, 1933, p. 213.

- (4-7) The corrected compositions of the liquid reaction products.
 (8) The yield of gaseous reaction products, calculated as a percentage by weight of the base material.
 (9-10) The content of hydrogen and paraffins of the reaction gas.

TABLE 1.—DATA RELATING TO THE AROMATISATION OR DEHYDROGENATION OF VARIOUS BASE MATERIALS.

Base Material.	Liquid Reaction Product.				Gaseous Reaction Products.		
	Per Cent. Wt. on Intake.	Per Cent. Vol. of Components of Same Number as Carbon Atoms as Starting Material.	Gross Composition, Per Cent. Wt. (Reduced to Standard Catalyst Activity).			Per Cent. Wt. on Intake.	Composition, Per Cent. Vol.
			Aromatics.	Naphthenes.	Olefines.	Paraffins.	
<i>n</i> -pentane . . .	86	about 93	3	0	22	75	83.1*
<i>n</i> -hexane . . .	88	" 99	19½	2½	16	62	93.6
2-methyl pentane . . .	87	—	5	0	33	62	95.5
<i>n</i> -heptane . . .	83	about 98	36	1	11	52	94.9
2-methyl hexane . . .	89	" 98	31	0	20	49	97.1
<i>n</i> -octane . . .	86	" 95	46	0	10	44	93.1
3-methyl heptane . . .	85	" 93	35	0	14	51	93.6
2-5-di-methyl hexane . . .	88	" 95	52	0	18	30	95.8
2-2-4-tri-methyl pentane . . .	90	" 92	3	0	26	71	94.0
<i>n</i> -nonane . . .	89	" 89	58	(o)†	15	27	93.5
<i>n</i> -hexene-1 . . .	86	—	31	(o)†	39	30	92.3
<i>n</i> -hexene-2 . . .	87	—	18	(o)†	67	15	87.9
<i>n</i> -heptene-1 . . .	83	—	—	—	—	—	92.7
<i>n</i> -heptene-2 . . .	88	—	—	—	—	—	94.2
<i>n</i> -octene-2 . . .	88	—	57	0	17	26	91.5
Cyclo-hexane . . .	86	about 99	40	58	2	0	98.6
Methyl cyclo-hexane . . .	86	—	49	48	3	(o)†	99.5
Cyclo-hexene . . .	85	about 99	73	3	24	(o)†	97.1

* Composition of gas effected by presence of uncondensed pentane.

† Assumed to be zero.

Further, some additional data for the *n*-heptenes and for *n*-heptane are given in Table II.

TABLE II.—SOME SUPPLEMENTARY DATA ON THE AROMATISATION OF THE HEPTENES.

Base Material.	Liquid Reaction Product.				
	Per Cent. Wt. on Intake.	Gross Composition, Per Cent. Wt. (Cat. C ₁₂).			
		Aromatics.	Naphthenes.	Olefines.	Paraffins.
<i>n</i> -heptane . . .	83	45	(0)	10	45
<i>n</i> -heptene-1 . .	83	69	(0)	9	22
<i>n</i> -heptene-2 . .	88	65	(0)	11	24

From these tables and from some additional observations the following conclusions may be drawn :

(1) **Yields and Material Balance.**—A scrutiny of the yields of liquid and gaseous reaction products will show that there is no considerable loss of material, indicating the absence of notable depositing of compounds of high molecular weight or carbon upon the catalyst.

(2) **Occurrence of Cracking and/or Synthesising Reactions.**—In addition to the foregoing, it is necessary to ascertain whether side reactions of a less extreme nature than carbonisation took place. Both our distillation data, from which column 3 in Table I was derived, and the composition of the reaction gases (content of paraffin hydrocarbons) induce us to make the following inferences :

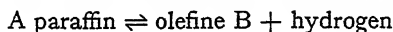
Cracking reactions only assume importance with hydrocarbons higher than C₈; cracking is somewhat more severe in the case of the olefines than in the case of the corresponding paraffins. The naphthenes examined underwent no appreciable cracking.

Formation of higher molecular weight compounds always occurs with base materials which are aromatised little or not at all (*e.g.*, 2, 2, 4-tri-methyl-pentane). With easily aromatised base materials no polymerisation reactions occur (*e.g.*, *n*-octane).

(3) **The Principal Reactions.**—All hydrocarbons whose structure permits direct formation of a six-carbon ring, or which contain a six-carbon ring, are aromatised to a marked extent; hydrocarbons whose structure does not allow of the direct formation of a six-carbon ring are not appreciably aromatised.

If the hydrocarbons are divided into two groups, one with a carbon skeleton permitting aromatisation and one not directly permitting aromatisation, we obtain the picture of the principal reactions shown in Table III.

Now it is clear that the reactions $A \rightarrow B$ and $B \rightarrow A$, *viz.*,



indicated in our diagram on page 993, are both realised under the influence of Cr₂O₃- catalyst.

As we have not been able to prove the presence of a *notable* quantity of naphthenes in our cyclisation products, either the courses indicated by ACD and by BCD are not realised at all, or CD is traversed at very great rapidity as compared with the other courses.

Consequently, the reaction scheme can be simplified as follows :

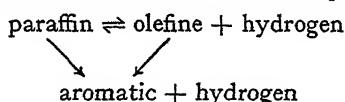


TABLE III.

	Hydrocarbons whose Carbon Skeleton Permits Aromatisation.	Hydrocarbons whose Carbon Skeleton does not Permit Aromatisation.
Paraffins.	1. Aromatisation.	1. Dehydrogenation to the corresponding aliphatic mono-olefine.
	2. Dehydrogenation to the corresponding aliphatic mono-olefine.	2. Formation of products of higher molecular weight.
Aliphatic olefines.	1. Aromatisation.	(Not investigated.)
	2. Hydrogenation to the corresponding paraffin.	
Cyclo-olefine.	1. Aromatisation.	(Not investigated.)
	2. Hydrogenation to the corresponding naphthene.	
Naphthenes.	Aromatisation.	(Not investigated.)

(4) **Quantitative Relationships in the Aromatisation of Aliphatic and Alicyclic Hydrocarbons.**—As we are inclined to ascribe the slight variation in yields of liquid reaction product (87 ± 3 per cent. weight) not so much to intrinsic causes as to incomplete condensation and experimental handling losses of material, the composition of the reaction products at once gives an excellent comparative picture of the degrees of conversion.

If we study Tables I and II a little more closely the following conclusions are arrived at :

(a) Under the given conditions aromatisation increases in the order of the series : paraffin—corresponding aliphatic olefine—corresponding six-ring naphthene—corresponding cyclo-olefine.

(b) Within each of these hydrocarbon groups aromatisation increases with the number of carbon atoms (Table IV).

TABLE IV.

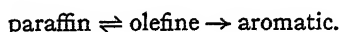
Table.	Paraffin.		Aliphatic Olefine.		Naphthene.	Cyclo-olefine.
	I.	II.	I.	II.	I.	I.
C ₆	19½	—	31 *	—	40	73
C ₇ {	36	—	—	—	49	—
C ₈	—	45	—	69 *	—	—
C ₈	46	—	57 †	—	84 †	—
C ₉	58	—	—	—	—	—

* α -olefine.

† β -olefine.

‡ Result of an additional experiment, not mentioned in Table I.

These rates of conversion of paraffin and corresponding olefine correlate with that which the basis of the following reaction mechanism would lead us to expect:



Taking into consideration the rates of conversion of olefine and naphthene, it is unlikely that the latter would really act as an intermediate product and yet hardly ever be recovered in the reaction product. We must, however, allow for the possibility that a naphthene of unstable form, "in statu nascendi," is formed at first and then dehydrogenates very rapidly to an aromatic.

(c) Branching of the carbon chain may either diminish or increase the suitability for aromatisation (Table V).

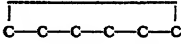
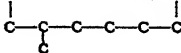
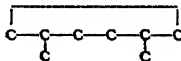
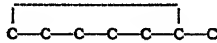
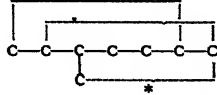
TABLE V.

<i>n</i> -heptane	36
2-methylhexane	31
<i>n</i> -octane	46
3-methyl heptane	35
2,5-di-methyl hexane	52

A more instructive picture of the possible effect of chain branching is obtained when the hydrocarbons are arranged according to an equal number of carbon-atoms in the longest chain (Table VI).

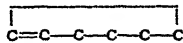
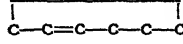
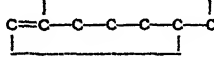
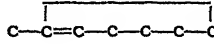
(d) In the aromatisation of olefines the position of the double bond in the molecule may be of great influence on the amount of conversion obtained (Table VII).

TABLE VI.

Paraffin.	Reaction.	Aromatisation.
<i>n</i> -hexane		19½
2-methyl hexane		31
2,5-dimethyl hexane		52
<i>n</i> -heptane		36
3-methyl heptane		35

* This reaction possibility is not realised, see p. 1002.

TABLE VII.

Olefine.	Reaction.	Aromatisation.	Hydrogenation.
<i>n</i> -hexene-1		31	30
<i>n</i> -hexene-2		18	15
<i>n</i> -heptene-1		69	22
<i>n</i> -heptene-2		65	24

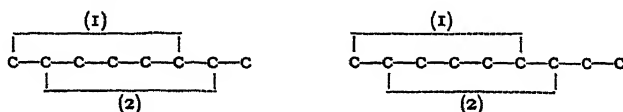
5. Comments on the Mechanism of the Principal Reactions in Aromatisation.

A. Identification of the Aromatics Formed.—(1) It has already been inferred above from Tables I and II that marked aromatisation only takes place in those cases where the carbon skeleton of the base material allows of the direct formation of a six-carbon ring (compare p. 999). The conclusion which may be drawn from this fact, *viz.*, that the Cr_2O_3 catalyst under the given circumstances does not effect isomerisation of the carbon skeleton, is confirmed by the results of a number of identifications of aromatics formed (Table VIII).

Consequently, except for lower aromatics originating from cracking reactions, practically no incongruous aromatic components were found.

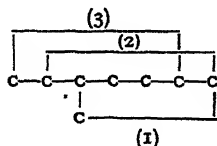
(2) In those cases where more possibilities for direct ring closure are present, these are apparently not all realised.

Of the two possible reactions



of which (1) yields ethyl benzene and *n*-propyl benzene respectively and (2) yields *o*-xylene and *o*-methyl ethyl benzene, it appears that (2) is far more likely to occur than (1)

Of the three conceivable reactions



of which (1) yields ethyl benzene, (2) yields *o*-xylene, and (3) yields *p*-xylene, (2) and (3) appear to occur almost exclusively (in roughly equal proportions).

The conclusion which might be drawn from these facts is that in cyclisation preferentially *secondary* carbon atoms participate in the ring

closure. This conclusion may probably be extended to the following rule: the aromatics formed in the cyclisation of aliphatic hydrocarbons contain the shortest possible side chain(s).

TABLE VIII.

Base Material.	Aromatics which can be Formed by Direct Ring Closure.	Individual Aromatics Experimentally Identified.
<i>n</i> -hexane	benzene	~ 100 per cent. benzene ^(a) *
<i>n</i> -heptane	toluene	> 95 per cent. ^(a) C ₇ -aromatic (toluene) ^(a) *
2-methyl hexane	toluene	~ 100 per cent. toluene ^(a) *
<i>n</i> -octane	ethyl benzene <i>o</i> -xylene	> 95 per cent. ^(a) C ₈ -aromatic ^(a) of which > 80 per cent. <i>o</i> -xylene ^(b) *
3-methyl heptane	ethyl benzene <i>o</i> -xylene <i>p</i> -xylene	~ 100 per cent. C ₈ -aromatic ^(a) of which 5 per cent. ethyl benzene ^(c) 35 per cent. <i>o</i> -xylene 5 per cent. <i>m</i> -xylene 55 per cent. <i>p</i> -xylene
2,5 dimethyl hexane	<i>p</i> -xylene	~ 100 per cent. C ₈ -aromatic ^(a) of which > 80 per cent. <i>p</i> -xylene ^(d) *
<i>n</i> -nonane	<i>n</i> -propyl benzene <i>o</i> -methyl ethyl benzene	~ 80 per cent. ^(a) C ₉ -aromatic ^(a) of which > 90 per cent. <i>o</i> -methyl ethyl benzene ^(c)

^(a) Quantities estimated from distillation data, etc.

^(b) Identified by and estimated from nitration and bromination results.

^(c) Identified by and estimated from oxidation experiments, carried out according to Moldawski.

^(d) Identified by and estimated from results of a nitration experiment carried out according to Reichel.

^(e) Remainder: lower molecular weight aromatics.

* These results fully confirm those of Moldawski and others.^{1, 2}

B. Identification of the Olefines Formed.—Table IX gives a summary of the results obtained in identifying the olefines in various reaction products.

TABLE IX.

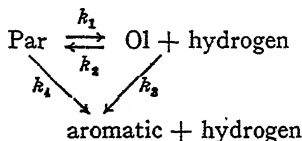
Base Material.	Olefine Identified in the Reaction Product.
<i>n</i> -pentane	<i>n</i> -pentene-2
<i>n</i> -hexane	mainly <i>n</i> -hexene-3
<i>n</i> -heptane	„ <i>n</i> -heptene-3
<i>n</i> -octane	probably <i>n</i> -octene-2 (— 3)
<i>n</i> -heptene-1	mainly <i>n</i> -heptene-3
<i>n</i> -heptene-2	„ <i>n</i> -heptene-3

The most striking point about these results is the fact that under the given reaction conditions, the Cr₂O₃ catalyst appears to catalyse a shift of the double bond to a more central position. For this reason the olefines isolated from the cyclisation products of *n*-hexane, *n*-heptane and *n*-octane may perhaps not be the primarily

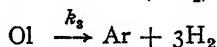
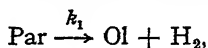
formed intermediate olefinic products, but are probably rearranged products.

Some Notes on Reaction-Kinetic Measurements.

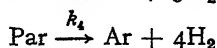
In our simplified reaction scheme :



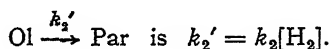
the reactions



and



are all monomolecular, whereas the reaction $\text{Ol} + \text{H}_2 \xrightarrow{k_2} \text{Par}$ is bimolecular. This reaction possibility can only be realised if hydrogen is present besides olefine; if the initial hydrogen concentration selected is so high that the removal of hydrogen during the reaction does not affect the total concentration of H_2 to a measurable extent, the reaction $\text{Ol} + \text{H}_2 \xrightarrow{k_2} \text{Par}$ may be regarded as a monomolecular reaction; for the reaction :



Now k_1 , k_2' , k_3 and k_4 may be determined by measuring the conversion of a paraffin to olefine and aromatic on the one side, and on the other side that of the corresponding olefine to paraffin and aromatic, at a certain temperature with a given catalyst in an atmosphere of hydrogen and at such a short time of contact that we may still speak of initial conversions.

For the present we carried out a number of determinations with the same type of catalyst and at the same temperature (465°C.) as described above, while *n*-heptane and *n*-heptene-2 were chosen as base materials; these hydrocarbons were conducted over the catalyst at atmospheric pressure in a stream of about 9 to 10 mols. of hydrogen per mol. of hydrocarbon.

As these measurements have not yet been completed and are to be continued with a greater degree of precision, we would only mention here that the results so far obtained point to the following conclusion: *the cyclisation of a paraffin largely proceeds through the dehydrogenation to a corresponding aliphatic olefine.*

Summary and Conclusions.

A large number of different hydrocarbons were passed over a pilled Cr_2O_3 -catalyst at 465°C. and atmospheric pressure, using a contact time of about twenty seconds (space velocity: about 3 per minute).

We measured the quantities and determined the composition of the average reaction products obtained during a period of five consecutive hours, the course of the reaction being followed with respect to the volume of gaseous reaction products formed.

As all the experiments were carried out under the standard conditions mentioned above, thus with a relatively long contact time, the "rates of reaction" determined were, naturally, not to be considered as true rate constants. However, as in none of our experiments a complete conversion (approaching the ultimate "equilibrium") was obtained, the results found

not only give a general impression of the nature of the reactions that have taken place, but also furnish a rough idea of the magnitudes of the reaction velocities.

The results of these experiments lead to the following conclusions :

(1) Hydrocarbons whose structure permits direct formation of a six-carbon ring, are aromatised to a marked extent.

(2) Hydrocarbons whose structure does not allow of the direct formation of a six-carbon ring, are not appreciably aromatised.

(3) The following table specifies in a simple way the principal reactions which generally occur :

	Hydrocarbons whose Carbon Skeleton Permits Aromatisation.	Hydrocarbons whose Carbon Skeleton does not Permit Aromatisation.
Paraffins.	1. Aromatisation.	1. Dehydrogenation to the corresponding aliphatic mono-olefine.
	2. Dehydrogenation to the corresponding aliphatic mono-olefine.	2. Formation of products of higher molecular weight.
Aliphatic olefines.	1. Aromatisation.	(Not investigated.)
	2. Hydrogenation to the corresponding paraffin.	
	3. Shift of the double bond to a more central position.	
Cyclo-olefines.	1. Aromatisation.	(Not investigated.)
	2. Hydrogenation to the corresponding naphthene.	
Naphthenes.	Aromatisation.	(Not investigated.)

(4) Besides the above-mentioned principal reactions, the cyclisation of the paraffins and olefines with eight and more carbon atoms also involves more or less extensive cracking reactions.

Cracking increases with the number of carbon atoms ; in the case of the olefines it is somewhat more pronounced than with the corresponding paraffins.

The naphthenes examined underwent no appreciable cracking.

(5) The degree of aromatisation of the aromatic-forming hydrocarbons increases in the following order : paraffins, corresponding aliphatic olefines, corresponding six-ring naphthenes, corresponding six-ring cyclo-olefines.

The differences between any two successive types in this series are all of the same order of magnitude.

(6) As the reaction products of the aliphatic hydrocarbons contained practically no naphthenes, it may be deduced (also on the basis of the preceding conclusion) that the cyclisation reaction does not involve the formation of six-ring naphthenes as (stable) intermediate products.

(7) In each of the hydrocarbon groups mentioned in conclusion 5, aromatisation increases with the number of carbon atoms.

(8) Branching of the carbon chain may either decrease or increase the aromatisation tendency.

(9) In the aromatisation of olefines, the degree of conversion may largely depend on the position of the double bond in the molecule.

(10) Apart from the formation of lower aromatics (through a cracking reaction), the aromatisation proceeds as simple ring closure without isomerisation of the carbon skeleton ; preferentially, secondary carbon atoms participate in the ring closure.

(11) Under the reaction conditions applied, Cr_2O_3 was found to catalyse the shift of the double bond in an olefine to a more central situation. Thus, the olefines present in the reaction products invariably contained a centrally situated double bond.

We are greatly indebted to Dr. J. Smittenberg for many valuable suggestions during this investigation, to Mr. W. L. Ghijsen for carrying out the gas analyses according to Scheffer-Mulders, to Mr. P. L. Kooijman for developing the ingenious method of feeding the hydrocarbons to the apparatus at a constant rate, and to the N. V. De Bataafsche Petroleum Maatschappij for permission to publish these data.

GENERAL DISCUSSION.*

Dr. D. D. Eley (*Manchester*), said: According to Wynne-Jones and Eyring¹ we may write a velocity constant as

$$k = \kappa \cdot \frac{kT}{h} e^{\frac{\Delta S'}{R}} e^{\frac{-\Delta H'}{RT}} \sim 10^{13} e^{\frac{\Delta S'}{R}} e^{\frac{-\Delta H'}{RT}}$$

where $\Delta S'(\Delta H')$ refers to the difference in entropy (heat content) between the initial and transition states of the reaction. In general the catalytic action of a surface upon a particular slow process, where the reaction paths in the gas phase and on the surface are at all comparable, is to be explained by a lowering of $\Delta H'$ consequent upon the chemisorption of the initial reactants and the transition complex upon the catalyst. In certain instances, *e.g.*, where a change in multiplicity occurs and κ may be smaller than unity (in most cases it is assumed to be unity as in the above equation), we might expect an increase in κ under the influence of a surface. In the case of a ring closure, however, we should expect the catalyst to

have a function, which may be important, in increasing the factor $e^{\frac{\Delta S'}{R}}$. For ring closure of a hexyl radical in the gas phase we have ¹ $\Delta S' = -25.6$ cal. deg.⁻¹ mole⁻¹, corresponding to a steric factor of 2.5×10^{-6} . When the hexyl radical is firmly bound to a surface, so that rotations are considerably restricted, we might expect the initial and transition complexes to have much the same entropy and so $-\Delta S'$ will be much smaller, corresponding to, say, a steric factor of 10^{-1} . The restriction on the reaction from the entropy standpoint has now been shifted to the preliminary stage of adsorption equilibrium; we should expect complicated molecules to have a low probability on a surface corresponding to the loss of rotations in the adsorption layer. In general we can say that the function of a catalyst surface on any slow process is to tend to bring the factor $e^{\frac{\Delta S'}{R}}$, whatever its value in the gas phase, towards unity. Owing to lack of knowledge of surface areas and surface reactant concentrations, it is impossible at present to test this suggestion.

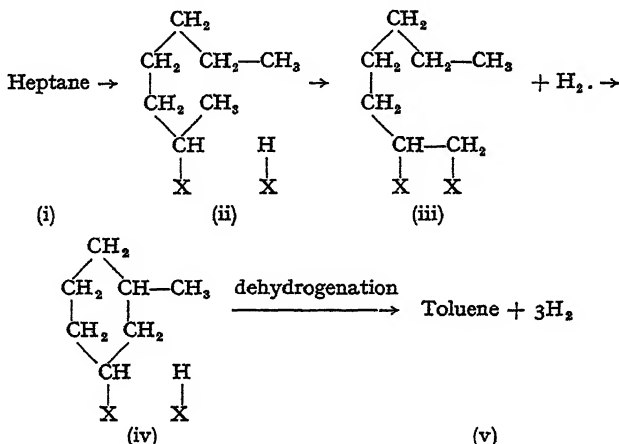
Dr. G. H. Twigg (*Cambridge*), said: I was very glad to hear from Evans that support for the associative mechanism for exchange in olefines was forthcoming from theoretical considerations. As an example of what Evans said about the relative probabilities of the two mechanisms one might instance the fact that exchange between ethylene and deuterium has been detected at as low as -80°C. , whereas exchange between ethane and deuterium which proceeds through dissociation is very slow at 100°C. on a bulk catalyst.

With regard to the paper by Pitkethly and Steiner, I should like to propose an alternative mechanism for the cyclisation process. This

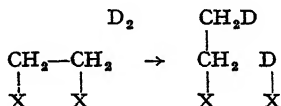
* On the three preceding papers.

¹ Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, 3, 493.

paper and that of Hoog, Verheus and Zuiderweg seem to prove conclusively that heptene is an intermediate between heptane and toluene. Mechanism (B) of Pitkethly and Steiner involves cyclisation from the half hydrogenated state. Their complete mechanism is thus heptane \rightarrow heptene \rightarrow half-hydrogenated state \rightarrow cyclic compound \rightarrow toluene. But this implies that the dehydrogenation heptane \rightarrow heptene goes through the simultaneous loss of two hydrogen atoms from the heptane molecule, whereas there is evidence² that dehydrogenation goes through a half-hydrogenated state. The following scheme is proposed to overcome this difficulty and still allow heptene to be an intermediate: heptane (i) \rightarrow half-hydrogenated state (ii) \rightarrow heptene (iii) \rightarrow cyclic compound (iv) \rightarrow toluene (v); and the following mechanism for it is suggested:—

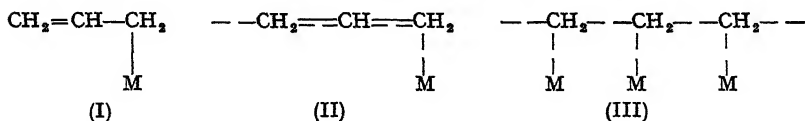


This mechanism accounts for the fact that no methyl cyclohexane is ever found during cyclisation, as, throughout the process, the molecule is continuously chemisorbed to the surface. The cyclisation step (iii) \rightarrow (iv) is exactly analogous to a step in the exchange reaction between ethylene and deuterium,



with here the CH_2 group taking the place of the D_2 molecule.

Dr. F. C. Frank (Cambridge) said: In an earlier part of the discussion Jost pointed out that one should not too readily dismiss the possibility of adsorption of $\text{CH}_2=\text{CH}-\text{CH}_3$ by dissociation of an H at the aliphatic carbon, because "resonance" occurs in the $\text{CH}_2=\text{CH}-\text{CH}_2$ radical. Evans objects that the resonance energy would not be available in the adsorbed state (I). I think that Jost only intended his proposal as a



warning against supposing too soon that one has eliminated all unwanted alternatives, and in the same sense I should like to hold that Evans' objection is not conclusive. It must be remembered that a metal is

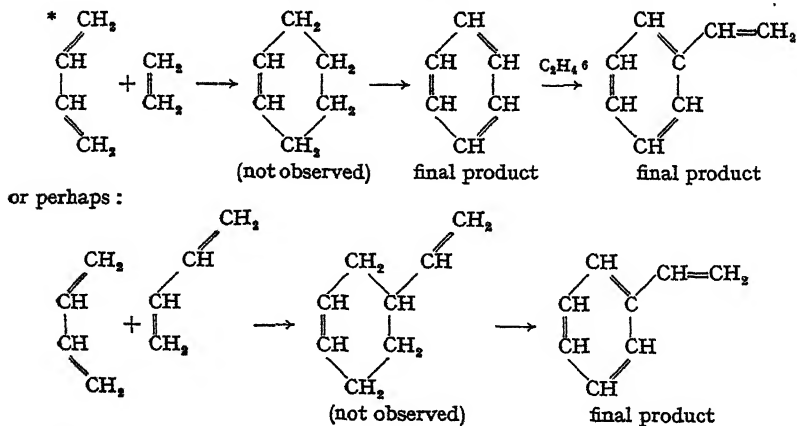
² Rideal, *Proc. Camb. Phil. Soc.*, 1939, 35, 130.

itself a "resonant system" and a "resonant system" of carbon atoms is in a sense metallic, so that the bond between the two may well be peculiar. Such a construction as (II) is no less defensible than Craxford's system (III).

Dr. G. R. Schultze (Berlin) (*communicated*): Hoog reported many interesting facts which shed some light upon the mode of cyclisation of aliphatic hydrocarbons. He and his collaborators were unable to find any notable quantities of naphthenes when aliphatic hydrocarbons were subjected to cyclisation. I can corroborate their results by referring to certain experiments³ we carried out on the condensation of ethylene. Applying short contact times in a flow system at temperatures from 700° to 800° C., this reaction proceeds through the formation of butadiene which subsequently reacts with another ethylene molecule to give benzene and styrene, apparently by the way of a Diels-Alder mechanism.* One would expect to find cyclic olefins as intermediary substances amongst the reaction products, especially since Küchler⁴ was able to prove for the reverse reaction that butadiene and ethylene are main products in decomposing cyclohexene. Yet we found no cyclohexene in any appreciable quantities. It appears that in Hoog's experiments,⁵ as well as in our own the cyclo-olefinic state is passed over very rapidly. This is quite surprising in view of Küchler's results, since dehydrogenation to benzene seems to be blocked for the non-catalytic course of reaction. Some unstable form of the primary cyclisation product as suggested by Hoog, might serve to reconcile this apparent discrepancy with the experimental facts.

Dr. H. Steiner (Sunbury-on-Thames) said: With regard to the paper by Hoog, Verheus and Zuiderweg, there are two points which I should like to raise. The first is the observation that branched chains cyclise more easily than straight chains. In most of the cases which they cite, a simple explanation is found in the greater number of possible modes of cyclisation occurring in branched chains. To quote examples from their Table IV, 2-5-dimethylhexane has four possible ways of cyclising but 2-methylhexane has only two, consequently the former substance cyclises more readily.

The second point concerns the migration of double bonds prior to



³ M. Schultze and G. R. Schultze, *Oel u. Kohle*, 1939, 15, 193, 215 and 233.

⁴ L. Küchler, *Nachr. Ges. f. Wiss. Göttingen, Neue Folge* 1, 1939, 237, and his report at this meeting.

⁵ Compare the results of A. and L. Farkas, Pitkethley and Steiner. This Discussion.

⁶ Berthelot, *Ann.*, 1867, 142, 257; and G. R. Schultze, *Ztschr. Elektrochem.*, 1936, 42, 676.

cyclisation. Whichever of the proposed mechanisms of cyclisation one accepts, it is clear that only those olefins can cyclise which have the double bond in at least the 5- or 6-position in the chain undergoing ring-closure. For other olefins the shifting of the double bond must constitute an intermediate step in the reaction. As pointed out in our paper, there seems to be some indirect evidence in our experiments that, under the given conditions, equilibrium of the different olefins is established owing to their rapid interconversion. I was very glad to find in this paper direct evidence for this view. As mentioned in their Table IX, starting with heptene (1) or (2) they found invariably heptene (3) in their products. This is the olefin one would expect from equilibrium considerations, which indicate that olefins with the double bond in the centre of the chain are formed preferentially. According to this view there should also be no difference in the rate of cyclisation of the isomeric olefins. However, the experimental evidence on this point is conflicting. According to Taylor and Turkevitch there is no difference in the cyclisation rate of *n*-heptene (1) and (3) and Hoog, Verheus and Zuiderweg found the same for *n*-heptene (1) and (2). However, they remarked a very pronounced difference in the cyclisation rate of *n*-hexene (1) and (2).

Dr. G. R. Schultze (*Berlin*) said: In the present discussion the problem of isomerisation has been treated mainly as a catalytic process. One may justly ask whether isomerisation takes place without catalysts being present. K  chler reported absence of isomerisation processes in connection with his work on homogeneous decomposition of cyclic hydrocarbons. We have studied the possibility of isomerisation for the homogeneous decomposition of butanes.⁷ Neither butane nor isobutane isomerises without presence of catalysts when heated to decomposition temperatures. Isomerisation in these cases seems to be linked to the catalytic course of reaction.

Referring to the paper of Waterman, I should like to inquire into the method of molecular weight determinations. The accuracy of the ring method of hydrocarbon analyses depends upon the reliability of molecular weight measurements, although the curves giving the specific refraction as a function of mean molecular weight are rather flat, *i.e.*, are not very sensitive to any change in the latter. Now, it is well known that the mean molecular weight of an oil depends strongly upon the oil concentration used in carrying out this test. In addition to this regular influence of concentration, rather irregular, broad variations almost up to 10 per cent. of the absolute value of molecular weight are observed owing to minor changes in the experimental procedure. To what extent may these two factors influence the accuracy of ring analyses and what method for determining molecular weights does he consider to be best for this particular purpose?

Dr. G. Salomon (*Delft*) said: According to Evans, well-known statistical considerations should be taken into account for the aromatisation of olefines on catalysts. From the study of ring closure condensation-reactions, however, it seems likely that a retardation effect is most characteristic for ring-closure reactions on surfaces.

The influence of substituents on the reactivity of primary, secondary and tertiary C—H and C—Cl bonds has been calculated by Evans and leads to valuable conclusions of a general nature. It is not very clear that these regularities are identical with those found in experimental organic chemistry, in which conclusions drawn from yields may correspond to differences in rates as small as 1 : 2 or 1 : 4. Moreover, for reactions in the liquid state, other factors such as the solubility and miscibility of the reaction products may determine the rate.

Dr. H. Hoog (*Amsterdam*) said: Prof. Rideal mentions a divergence of view to the mechanism of the cyclisation reaction between Pitkethly

and Steiner and ourselves. If we disregard the interpretation of the results with reference to what happens on the surface of the catalyst, I see no real difference between the *results* of Pitkethly and Steiner and our own; we both come to the conclusion that in cyclisation—in a certain range of contact times—aliphathic olefine formed is removed just as quickly as it was formed. In our opinion the authors should have drawn the conclusion from this reaction scheme



and should have laid their curve through the points of measurement as shown in Fig. 1. For, with an extremely short contact time, the olefine concentration is still equal to zero and therefore

$$\frac{dO}{dt} = k_1[P] - k_2[O] = k_1[P].$$

The angle α therefore has a finite value. On the other hand,

$$\frac{d[A]}{dt} = K_2[O] = 0.$$

In other words, the aromatic curve touches the time axis in the origin.

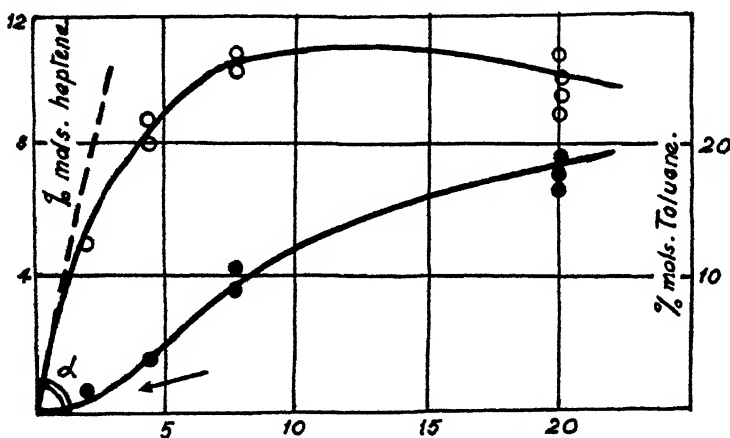


FIG. 1.

Referring to Taylor and Turkevitch's experimental results I should like to draw your attention to the following point: from their paper one would conclude that several olefines whose structure does not allow of the direct formation of a six carbon ring, may yet be considerably aromatised. Recently, however, Verheus carried out an experiment upon another olefine of this type: 2:4 dimethyl pentene -2, and observed practically no aromatisation at 465° C. and a contact time of 20 sec. Can Taylor indicate any cause of this discrepancy in the method of analysis used by him and by ourselves (hydrogenation followed by sulphonation) or does he see some other cause for this disparity?

In another point there is a difference between the results of Taylor and Turkevitch and our own: we found a distinct difference in the rate of aromatisation of hexene-1 and hexene-2 (both experiments carried out in duplicate) and from considerations of analogy we should expect a similar difference to exist between the rate of aromatisation of heptene-2 (equal to that of heptene-1) and heptene-3. Taylor and Turkevitch, however, find an even somewhat larger aromatisation conversion for heptene-3 than for heptene-1.

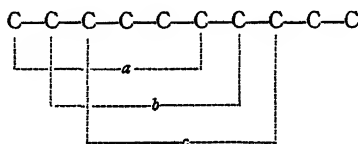
We are not able to give an explanation for these phenomena. Does Taylor think it conceivable that the situation in the case of C_7 differs from that in the case of C_6 and that for example the mobility of the double bond is much larger in C_7 than in C_6 ?

Finally I wish to say, with regard to our own work:—

On page 1003 we have endeavoured to generalise the conclusion that "in cyclisation preferentially secondary carbon atoms participate in the ring closure," to the rule "the aromatics found in the cyclisation of aliphatic hydrocarbons contain the shortest possible side chains."

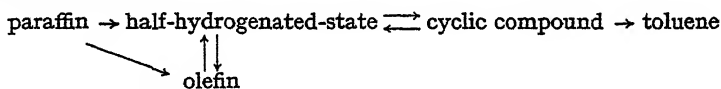
It has since been found that this generalisation is incorrect: in some experiments carried out by Verheus with *n*-decane as the base material it was found that a very small portion of the aromatics formed consists of naphthalene and the greater part of a di-alkyl aromatic, which was identified as *o*-methyl propyl benzene on the strength of its physical constants.⁸

Of the three possibilities (a), (b), (c)



the one leading to the shortest possible side chains—(c), giving di-ethyl benzene—is the one that has *not* been realised.

Dr. H. Steiner (*Sunbury-on-Thames*), in reply, said: In reply to Twigg I should like to point out that in the reaction sequence given in our mechanism B:



we left it open whether the half-hydrogenated state is formed directly from the paraffin or *via* the olefine, thus it is immaterial to the mechanism whether dehydrogenation is a one-stage or a two-stage process.

I should like to add that although at present it is not possible to decide for one or the other of the alternative mechanisms proposed, it should be possible to exclude at least some of the possibilities for reacting by comparing the rates of dehydrogenation and cyclisation on the one hand with exchange reactions and double bond migration on the other hand on the same catalyst and with the same substrate as feed.

Finally, I want to say that we are in complete agreement with Hoog as regards his interpretation of our results on dehydrogenation and cyclisation at small conversions, before the stationary state is established, and we are grateful to him for drawing our attention to this point, which we had overlooked.

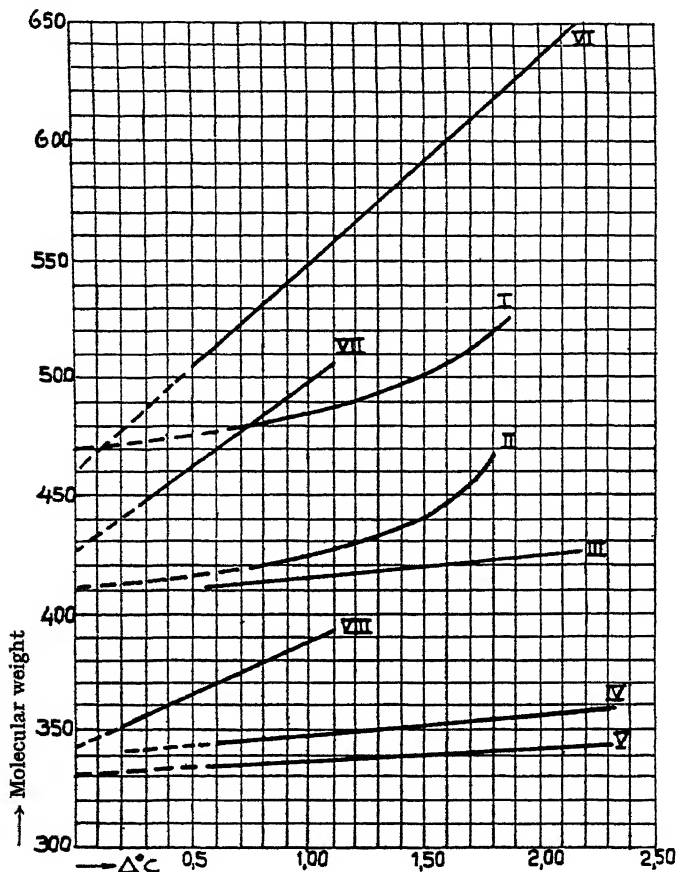
Prof. H. I. Waterman (*Delft*), in reply, said: In a paper of J. C. Vlughter, H. I. Waterman and H. A. van Westen,⁹ the methods which are applied in the laboratory of chemical engineering of Delft University for determining the molecular weight are described. It will be seen that with natural oils, or products obtained therefrom, the values found approximate to the correct molecular weight. Only for paraffins or oils very rich in paraffins are the values found slightly too high. In the figure, I represents a paraffin base oil, II a Rangoon paraffin wax, and III, IV and V are oils rich in rings. Naphthalene was used as a solvent in these experiments.

In research work carried out later it was found that fractions of *iso*-butene polymers show larger deviations in naphthalene content, if 1.0° C.

⁸ U.O.P. Booklet No. 217.

⁹ *J. Inst. Pet. Tech.*, 1935, 21, 673.

is taken for the depression of the freezing-point (curves VI, VII and VIII). For polymers with a molecular weight of, *e.g.* 350 and lower, these deviations were much smaller. For the *isobutene* polymers much better results could be obtained by the use of very pure cyclohexane. The low heat of melting of cyclohexane presents, however, a special care. The necessary



precautions which have to be taken in this case have been described elsewhere.¹ The results thus obtained were very satisfactory. Therefore for this type of high molecular weight polymers, cyclohexane can be recommended for cryoscopic molecular weight determinations.

For further details, the original papers cited may be consulted.

SECTION D. COMBINATION OF SATURATED HYDROCARBONS AND OLEFINES.

SOME PROBLEMS ASSOCIATED WITH OLEFINE-ISOPARAFFIN ADDITION REACTIONS.

By S. F. BIRCH and A. E. DUNSTAN.

Received 4th April, 1939.

The addition of olefines to paraffins to give higher paraffins represented by



has been accomplished in three ways:—

- (1) by heat and pressure alone,
- (2) with the aid of activated halide catalysts and,
- (3) by means of sulphuric acid.

Of these methods the last, which is applicable only to the reaction of olefines with *isoparaffins*, is of considerably technical significance since it enables *isoparaffins* of a type especially suited for use in aviation fuels to be readily produced from petroleum gases. It is also of academic interest since it disposes of the view, long held by chemists, that paraffins are inert and non-reactive.

Some account of the experimental details and optimum conditions for carrying out these reactions has been given¹

The reaction is found to be general in character, and has been successfully applied to a variety of lower *isoparaffins* and olefines. Of the paraffins examined *isobutane*, *isopentane* and *isohexane* (2-methylpentane) react readily, but *iso-octane* (2.2.4-trimethylpentane) fails to do so. The olefines investigated include propene, butene-1 and butene-2, *isobutene* and its di- and tri-merides, the butene-*isobutene* codimer and trimethylethylene; all these react smoothly and give excellent yields of *isoparaffinic* products.

No evidence has yet been obtained that the reaction is applicable to any but the simpler *isoparaffins*. Attempts to combine di-*isobutene* with *n*-butane and butene-2 with 2.2-dimethylbutane gave only the products ordinarily obtained when the olefines alone are treated with acid under the same conditions.

Careful fractionation of the product from any of the addition reactions shows it to be a complex mixture of *isoparaffins* boiling over the range 27-185° C.* together with a relatively small residue consisting of high-boiling *isoparaffins* and olefines, in which the former usually predominate.

From the wide boiling range of the *isoparaffins* formed it is obvious that the reaction is not confined to simple addition, since there are formed hydrocarbons containing numbers of carbon atoms both more and less

¹ Birch, Dunstan, Fidler, Pim and Tait, *J. Inst. Pet. Tech.*, 1938, **24**, 308-20; A.C.S. Meeting, Milwaukee, 1938; A.C.S. Meeting, Baltimore, 1939.

* The normal motor spirit range.

than would be expected on this basis. The formation of these can only be explained on the assumption that secondary reactions of a complex nature are also involved. Furthermore, the primary reaction itself may produce one or more isomers depending upon the manner in which addition takes place, and this may add further to the complexity of the product.

This is well illustrated by the work of Frey and Hepp,² who found that under the influence of heat and pressure alone, the addition of ethylene to propane resulted in the formation of both *iso*- and *n*-pentanes depending upon whether the addition mechanism involved either a primary or secondary carbon atom in the propane molecule.

The close similarity in the composition of the products obtained from *isobutene* and its polymers and co-polymers indicates that depolymerisation occurs before addition. Furthermore, since both *isobutene* and the normal butenes also yield closely similar, if not identical products, it appears that isomerisation of the olefine to the branched form also takes place before addition to the *isoparaffin*.

Possible secondary reactions which may affect the products include isomerisation, degradation and addition to them, or to products derived from them, of further olefine molecules. These reactions, particularly those responsible for the formation of the higher and lower molecular weight *isoparaffins*, may be suppressed to a considerable extent by employing a large excess of the *isoparaffin*. Even under the most favourable conditions, however, a considerable part of the primary product may undergo secondary changes with the results that it is not always easy to determine whether a particular hydrocarbon is primary or secondary in origin.

It is thus obvious that the products obtained are the result of a number of different reactions, and that only by a careful study of the individual hydrocarbons formed from various pairs of olefine: *isoparaffin* reactants can any knowledge of these reactions be obtained. Such a task is a formidable one in view of the close similarity in physical properties of the isomeric hydrocarbons possibly formed. This often renders their separation and identification extremely difficult, particularly in view of the lack of reliable physical data for many of the more complex *isoparaffins*. Fortunately, in spite of the variety of reactants, the hydrocarbons which constitute the major reaction products appear to conform to certain types, the individual members of which are relatively well-defined and easy to identify. Useful information giving a clue to constitution is frequently furnished by the anti-knock value (octane number) particularly when two hydrocarbons of varying length of carbon chain have approximately the same physical properties. Unfortunately, the amount of material required for such tests is relatively large, and is of course lost in the process. This difficulty is being overcome to some extent by the use of Raman spectra. This method has already proved valuable in proving that two *isnonanes* formed in different reactions were identical.

Although the action of the acid in bringing about the reaction appears to be catalytic, in use the activity of the acid falls off, at first slowly and finally rapidly. During this period the acid becomes a light to medium brown in colour and increases in volume, slowly at first but rapidly at the stage when the activity eventually drops away. On

² *Ind. Eng. Chem.*, 1938, 59, 1768.

dilution of the acid with water there separates an oil which, from its general behaviour and properties, is highly unsaturated. Since it has not been possible to separate this oil from the acid by any means other than dilution (*e.g.*, extraction with solvents) it would appear to be in combination with the acid. The derivation of this unsaturated material is of considerable interest. It appears to be formed by a side reaction involving the acid and the olefine in which part of the latter, after being polymerised, becomes saturated at the expense of a further part of the polymer. Reactions of this type involving what has been termed "hydropolymerisation" were first observed by Ormandy and Craven,³ and later investigated by Nametkin and Abakumovskaya,⁴ and by Ipatiev and Pines.⁵ The oil separated from acid which has been stirred with di-*isobutene* shows a close similarity in properties to that obtained from acid which has been used in the di-*isobutene-isobutane* condensation. This leaves little doubt that the two have been similarly formed.

The amount of oil which can be separated from used acid indicates that under optimum addition-reaction conditions, the extent of hydropolymerisation is small. The acid-insoluble products of this reaction being high-boiling, must occur in the residue boiling above 185° C. and probably account for its unsaturated nature. The fact that such hydrogen-exchange reactions can and do take place under reaction conditions in the presence of sulphuric but not of phosphoric acid is regarded as highly significant and considered to have an important bearing on certain of the changes to be described. For example, the presence of considerable amounts, *i.e.*, 22 per cent. of butadiene in mixed butenes does not have the adverse effect upon the reaction with *isobutane* that would be expected. Little, if any change is observed in the composition of the reaction products, the only noticeable effect being more marked dilution of the acid. Since the yield of product is slightly improved it would appear that under the conditions of the reaction the butadiene becomes partially hydrogenated (presumably at the expense of the *isoparaffin*) to butenes which then react normally. Apparent confirmation for the dehydrogenation of the *isoparaffin* in this way is the formation in the reaction of propene with *isobutane* of appreciable quantities of 2.2.4-trimethylpentane—a normal product of the reaction of *isobutene* and *isobutane*—together with other *iso*-octanes. Since it is improbable that 2.2.4-trimethylpentane could have been formed from the primary products of the propene-*isobutane* reaction in any way, it must be assumed that some of the *isobutane* has been converted into *isobutene* which has subsequently reacted with the excess of *isobutane* present. The mechanism by which addition takes place in the presence of sulphuric acid is obscure. Frey and Hepp,² using heat and pressure alone, satisfactorily explained the formation of their products on a free radical mechanism. They found that the rate at which hydrogen is replaced by ethyl is dependent upon the nature of the carbon atom to which the hydrogen atom is attached, decreasing in the order tertiary—secondary—primary.

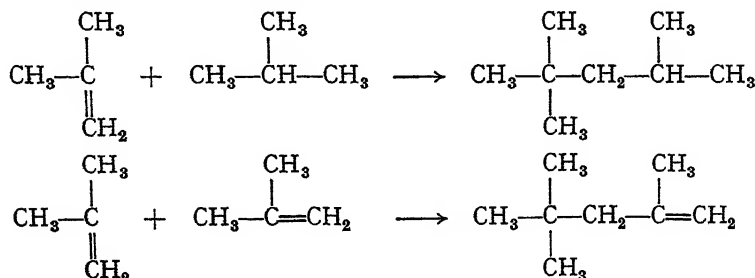
Not only does it seem unlikely that a similar mechanism could operate in reactions carried out in the liquid phase, but the products formed do not appear to conform with those to be expected on the basis of the above order of reactivity. Instead, the identity of the skeletal structure of the apparent main addition-product from *isobutene* and *isobutane*,

³ *J. Inst. Pet. Tech.*, 1927, 13, 311, 844.

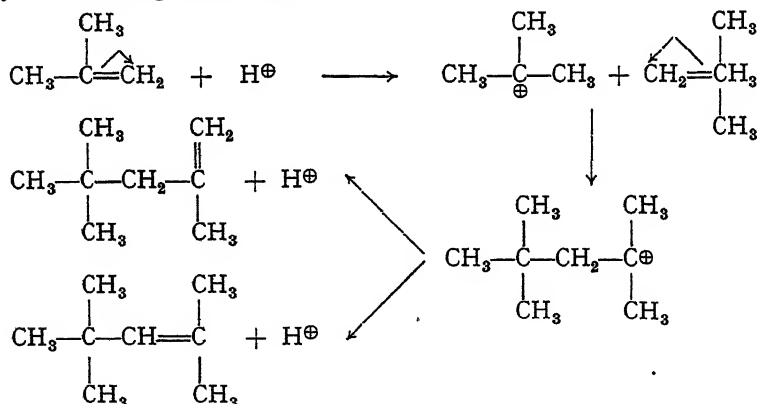
⁴ *J. Gen. Russ.*, 1936, 6, 1161.

⁵ *J. Org. Chem.*, 1936, 1, 477.

viz., 2.2.4-trimethylpentane, with that of di-*isobutene* suggests that a similar mechanism to that postulated by Whitmore⁶ for the polymerisation of *isobutene* may be involved.



According to Whitmore the first stage in olefine polymerisation is the addition to the olefine molecule of a proton derived from the acid, to form a positive fragment, which is then capable of reacting with a further olefine molecule in a manner similar to the original proton addition. The loss of a proton at this, or if polymerisation proceeds further, at some later stage results in the formation of an unsaturated linkage. The polymerisation of *isobutene* to form di-*isobutene* is thus represented by the following mechanism:—



Polymerisation of an olefine by an acid catalyst in the presence of an *isopara*ffin is alone insufficient to explain the mechanism of olefine-*isopara*ffin addition, since the polymerisation of *isobutene* by phosphoric acid in the presence of *isobutane* or *isopentane* gives no addition-products. It is therefore necessary to assume some activation of the *isopara*ffin by the acid before the addition reaction can occur. This may be brought about by some intermolecular association at the *isopara*ffin sulphuric acid interface, and such a suggestion receives considerable support from the observation that better oil-in-acid emulsion results in a better yield of condensation product. Indeed, effective dispersion of the oil in the acid is essential.

No references to the action of sulphuric acid upon *isopara*ffins other than of oxidation or sulphonation appear in the literature. Recently, Ingold, Raisin and Wilson⁷ have observed that an exchange reaction

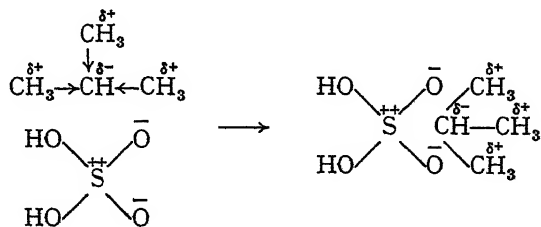
⁶ *Ind. Eng. Chem.*, 1934, 26, 94.

⁷ *J.C.S.*, 1936, 138, 1643; *cf.* also Raisin, Ph.D. Thesis, 1936 (University of London).

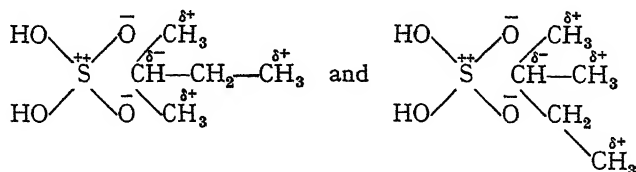
occurs between deutero-sulphuric acid and certain paraffinoid hydrocarbons. Both normal and *isoparaffins* were found to undergo deuteration at room temperature, this being accompanied in the case of the *isoparaffins* examined, 2,2,4-trimethylpentane and 2,5-dimethylhexane, by side-reactions. Since the hydrogen-exchange can be correlated with coloration of the acid, it is suggested that the reactive entity is identical in both reactions—a significant observation in connection with the breakdown of *isoparaffins* by sulphuric acid discussed later. To explain the mechanism of the exchange, Ingold and his co-workers postulate the formation of intermediate complex between the paraffin and acid. It is pointed out that such an hypothesis "carries certain implications concerning the orientation of the exchange; it should occur preferentially at those hydrogen-bearing carbon atoms which can acquire the strongest negative charge," *i.e.*, tertiary carbon atoms, and, after these at methylene groups adjoining the branching point of the skeleton. While this order of reactivity agrees with that observed by Frey and Hepp, it appears to be completely at variance with that obtained from the olefine-*isoparaffin* addition in the presence of sulphuric acid. Thus the addition of propane to *isobutane* yields 2,4- and 2,3-dimethylpentanes and not the anticipated 2:2:3-trimethylbutane. Similarly, from *isopentane* and butene-2 the product consists of 2,2,5-trimethylhexane. From these and other observations the conclusion is reached that addition tends to occur on the terminal methyl groups rather than at the tertiary carbon atom. To what extent addition may also take place on the methylene groups is difficult to say, since it has been found that the products which would be formed by such an addition from *isopentane* are readily broken down by the acid.

A further indication that the reactivity suggested by Ingold and his co-workers does not correspond with that observed in acid-catalysed olefine-*isoparaffin* addition is shown by methylcyclohexane which although undergoing deuteration with great readiness does not appear to react with olefines in the presence of acid.

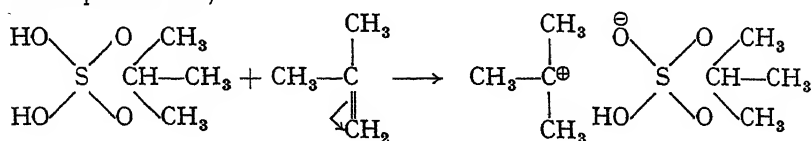
A possible alternative to Ingold's hypothesis is the formation of a complex between the *isoparaffin* and the acid as follows:—



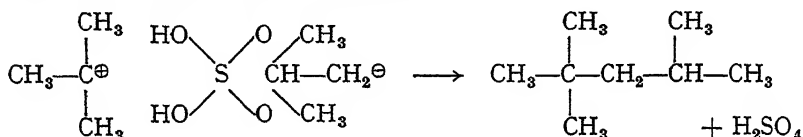
Similarly *isopentane* would form two complexes having different configurations:—



When an olefine molecule approaches the complex, the same active fragment is produced as in polymerisation, *i.e.*, a proton is gained from the sulphuric acid,



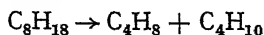
after which there will be a tendency for the sulphuric acid to regain a proton. It is suggested by the writers that this is obtained from the associated paraffin molecule, and furthermore from one of the methyl groups, in accordance with the known polarisation of the *isoparaffin* molecule. Under these conditions the rupture of the C—H bonds may be imagined to occur with small energy of activation provided the proton remains bound in the complex. The two charged hydrocarbon fragments then unite to give 2,2,4-trimethylpentane.



As has been pointed out above, secondary reactions play an important part in determining the nature of the products. For instance, it is known that many hydrocarbons which may be assumed to be primary products of addition are broken down on being stirred alone with concentrated sulphuric acid at ordinary temperatures; this results in a complex mixture of higher and lower *isoparaffins* together with acid-soluble compounds similar to those formed during hydropolymerisation reactions. The *isoparaffins* which have been observed to break down in this way include 2,2,4-2,2,3-, and 2,3,4-trimethylpentanes, 2,2,5-trimethylhexane and 2,3-dimethylbutane. Of these 2,3,4-trimethylpentane appears to be most easily attacked and 2,3-dimethylbutane the least. Under similar conditions *isopentane*, 2,2-dimethylbutane and 2,2,3-trimethylbutane do not appear to be affected.

The close similarity in the true boiling-point distillation curve of the product obtained from the addition of *isobutene* and *isobutane* with that obtained for the breakdown products of 2,2,4-trimethylpentane, the primary addition product of this reaction, suggests that most of the secondary products observed in the former reaction have been formed in this way.

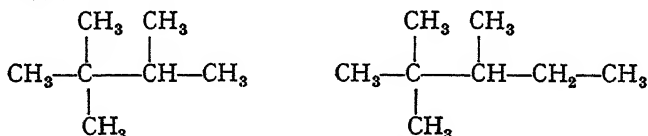
The action of sulphuric acid upon 2,2,4-trimethylpentane is first indicated by the development of a brown coloration which darkens rapidly as the reaction proceeds; the development of such a coloration closely resembles that associated by Ingold, Raisin and Wilson⁷ with hydrogen exchange. Since normal paraffins do not give a coloration when stirred with sulphuric acid unless they contain small amounts of olefines, it is possible that the darkening of the acid when certain *isoparaffins* are acid treated is actually an indication of olefine formation. The formation of appreciable amounts of *isobutane* when 2,2,4-trimethylpentane is treated with acid, coupled with the rapid darkening of the acid, suggests that the reaction



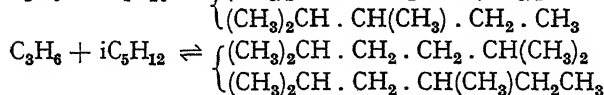
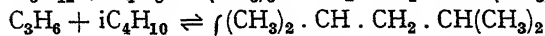
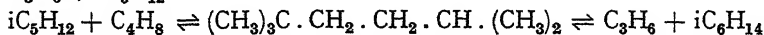
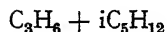
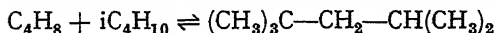
takes place, that is to say, that the addition reaction is to some extent reversible, and that certain *isoparaffins* can break down to give olefines and *isoparaffins*. Such a breakdown would appear to be confirmed by the presence in the acid layer of products similar to those obtained when *isobutene* and sulphuric acid react together.

In order to be able to forecast the secondary products in an olefine-*isoparaffin* addition, it is necessary to have some knowledge of the course of the degradation of *isoparaffins* by sulphuric acid. However, the information at present available concerning this fission is not yet sufficient to act as a basis for any hypothesis as to the breakdown mechanism. But it is certain that to account for many of the products isolated, breakdown must be preceded by rearrangement similar to that observed in the course of various dehydrations by Whitmore.⁸ Certain structures, containing strongly electronegative centres, appear to favour such fission, but that the presence in the molecule of one electronegative centre is not sufficient, is shown by the apparent stability of *isopentane* and 2.2-dimethylbutane.

It is clear that two electronegative centres in the molecule are necessary before fission can occur, and it appears that one of these centres must be tertiary in character. Thus, 2,3-dimethylbutane and 2.3.4-trimethylpentane both break down on treatment with sulphuric acid, the latter more readily on account of the abundance of electronegative centres in the molecule; 2.2.4-trimethylpentane, having a methylene group situated between a quaternary and a tertiary carbon atom, is also capable of undergoing fission, either before or after rearrangement to a 2.3.4-trimethylpentane structure. That the above are not the only conditions for breakdown to occur is shown by the fact that 2.2.3-trimethylbutane does not break down, whereas 2.2.3-trimethylpentane does.



Even less information is at present available concerning the formation of the higher molecular weight *isoparaffins* formed as secondary products. If it is assumed that fission of the primary product can in certain instances take place at more than one position in the molecule, it is obvious that a number of new hydrocarbons can be formed by the recombination of the fragments other than as originally combined. Such an hypothesis finds some confirmation in similar *isoparaffins* being formed from various pairs of reactants. Thus the following scheme would explain the formation of the various *isoparaffins* isolated from the butene-*isobutane* reaction.



⁸ *J. Amer. Chem. Soc.*, 1933, **55**, 1106, 4153.

TABLE I.—PRODUCTS FORMED IN VARIOUS OLEFINE-ISOPARAFFIN ADDITION REACTIONS.

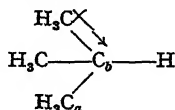
Isoparaffin.	Olefine.	Main Product.
<i>Isobutane</i>	Propene	2.4-, 2.3-dimethylpentane ; 2.2.4-trimethylpentane ; 2.3-dimethylbutane.
<i>Isobutane</i>	Butene-1 Butene-2 Di- <i>isobutene</i>	2.2.4-trimethylpentane ; 2.5-, 2.4-dimethylhexane ; 2.2.5-trimethylhexane ; 2.3-dimethylbutane ; 2-methylpentane (2.2.6-trimethylheptane ?) ; <i>isopentane</i> .
<i>Isopentane</i>	Propene	2.3-, 2.4-, 2.5-dimethylhexane ; <i>isobutane</i> .
<i>Isopentane</i>	Butene-2 Di- <i>isobutene</i>	2.2.5-trimethylhexane ; <i>isohexanes</i> (probably mainly 2-, 3-methylpentanes) ; (2.2.6-trimethylheptane ?).
2-Methylpentane	Butene-2 Di- <i>isobutene</i>	(2.2.6-trimethylheptane ?) ; <i>isobutane</i> ; <i>isopentane</i> .

Isomerisation of the original *isoparaffin* would explain the formation of such *isooctanes* as 2.3.4- and 2.3.3-trimethylpentane, the presence of which in the reaction is also suspected but has not been confirmed.

We wish to record our thanks to the Chairman of the Anglo-Iranian Oil Company, Limited, for permission to publish this account.

GENERAL DISCUSSION.

Dr. W. A. Waters (*Durham*) said: Since the above-described reactions between olefines and *iso*-paraffins occur in sulphuric acid at a low temperature they are probably different in type from the high-temperature free-radical reactions that have been dealt with hitherto at this meeting. One would expect that the highly polar reagent H_2SO_4 would bring about a reaction of an ionic type, and a paraffin hydrocarbon can only be converted into an active ionic reagent by a process of proton elimination.



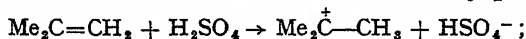
In a paraffin such as *iso*-butane the tertiary carbon atom (*b*) has a more electronegative environment than the atom (*a*) on account of the cumulative induced polar effect (+ F or - I) of the electrical dipoles associated with the methyl groups. Carbon atom (*b*) will therefore be more reactive than (*a*) if exposed to attack by an electropositive (electrophilic) reagent such as a halogen, and would more easily lose an attached group by dissociation as an anion (*e.g.*, facile hydrolysis of *tert.* butyl chloride).

On the other hand dissociation of an attached hydrogen atom as a cation, $\text{>C}_\alpha\text{—H} \rightarrow \text{>C}_\alpha^- + \text{H}^+$ would be *less* facile than for a methyl group, $\text{C}_\alpha\text{—H}$.

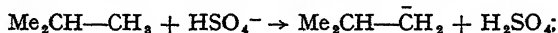
One would therefore anticipate that the order of proton release from paraffins should be $\text{CH}_3 > \text{CH}_2 > \text{CH}$ and it is amongst the *iso*-paraffin structures that methyl groups are most prevalent.

The addition reactions of Birch and Dunstan could thus be interpreted as :

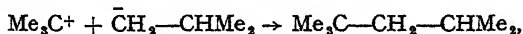
- (a) Whitmore's scheme for activation of olefines by proton addition



- (b) Ionisation of the *iso*-paraffin by proton release



- (c) Addition of the two reactive organic ions



giving a product of the structure of the hydrocarbon isolated experimentally.

Since the internal polar forces (*i.e.*, the local dipoles) in all paraffin hydrocarbons are very small in magnitude, one would not anticipate that the relative reactivities of the various parts of any hydrocarbon molecule would be so markedly different as to necessitate the occurrence of reactions of one type only. Even amongst the reactions of the more polar alkyl halides one finds that there occur changes between alternative reaction mechanisms which are so evenly balanced that two homologues may yet react in an entirely different manner.¹

The occurrence of similar anomalies in hydrocarbon reactions would not be surprising.

¹ Cf. *J. Chem. Soc.*, 1935, 244.

PART IV. OLEFINE POLYMERISATION.

SECTION A. DIMERISATION.

HEAVY METAL SULPHIDES AS CATALYSTS FOR THE POLYMERISATION OF OLEFINE HYDROCARBONS.

BY E. H. INGOLD AND A. WASSERMANN.

Received 21st March, 1939.

The most important catalysts for the conversion of the simple olefines into hydrocarbons boiling in the range of commercial gasoline are metals,¹ sulphuric acid,¹ metal halides,¹ supported phosphoric acid,² and certain phosphates.³ Metals are easily poisoned by sulphur compounds, sulphuric acid is corrosive and tends, except under carefully controlled conditions, to promote undesirable side reactions and metal halides, such as aluminium chloride or zinc chloride, produce relatively large quantities of heavy polymers together with the low boiling hydrocarbons. Supported phosphoric acid or phosphates, on the other hand, are not poisoned by sulphur, are non-corrosive solids, and produce a high yield of low boiling hydrocarbons unaccompanied by tar or pitch. The experiments now to be described deal with substances of similar properties.

It has been found that a typical diene synthesis, *viz.*, the dimerisation of cyclopentadiene, which is homogeneous in the gas phase and in various solvents⁴ becomes heterogeneous in the presence of the sulphides of certain heavy metals. The results of the measurements, which were carried out in paraffin solution, at atmospheric pressure and 155° C., are in Table I.

The majority of the black sulphides are catalytically active, while the white and yellow sulphides are inefficient under the conditions of our experiments. The activity of the same metal sulphide depends markedly on the method of preparation; this is probably due to the fact that impurities, *e.g.*, alkali sulphide, metal sulphate, metal oxide, sulphur or adsorbed oxygen, contribute to the observed effect.

Cupric sulphide is one of the most efficient catalysts of Table I and, therefore, an attempt has been made to use it for the polymerisation of other olefines. The first experiments with trimethylethylene were unsuccessful but using, instead of cupric sulphide, a mixture of cupric sulphide with sulphur or with cupric sulphate trimethylethylene could be catalytically converted into diamylene. The experiments of Table II were carried out at 100° in containers the volume of which was about 20 times larger than that of the liquid reactants; under these conditions sulphur or cupric sulphate alone were inactive. Cupric oxide or a mixture of cupric oxide and cupric sulphide had also no measurable effect.

The activating influence of sulphur was not observed if the cupric sulphide of catalyst No. 2 was prepared from cupric sulphate and hydrogen sulphide in acid solution. At the end of an experiment which was similar

¹ Cf. the references in Chapter III of "Polymerisation" by Burk, Thompson, Weith and Williams, New York, 1937.

² Ipatieff and Schaad, U.S.A. Patent 2,101,857; 2,102,073; 2,102,074.

³ Dunstan British Patent 460,659.

⁴ Cf. References in *Trans. Faraday Soc.*, 1938, **34**, 128; Benford and Wassermann, *J. Chem. Soc.*, 1939, 362; Benford, Kaufmann, Khambata and Wassermann, *ibid.*, 381.

to No. 4, the catalyst was separated from the liquid and used for another run; it was thus found that the activity was not decreased during the first reaction. The efficiency of catalyst No. 4 is not changed by the addition of 7 per cent. water, but sodium sulphide or sodium sulphate are powerful inhibitors. Similar results to those of Table II were obtained if instead of trimethylethylene commercial mixtures of amylenes were used.

TABLE I.—DIMERISATION OF *cyclo*-PENTADIENE.

Sulphide .	CuS	Cu ₂ S	Ag ₂ S	SrS	ZnS	CdS	HgS	Tl ₂ S	SnS ₂
Colour of sulphide	black	black	black	white	white	yellow	black	black	yellow
Catalytic Efficiency	+	+	+	—	—	—	+	+	—
Sulphide .	SnS	PbS	As ₂ S ₃	Bi ₂ S ₃	MoS ₂	FeS	FeS ₂	KFeS ₂	FeCuS ₂
Colour of sulphide	black	black	yellow	black	black	black	black	black	black
Catalytic Efficiency	+	+	—	+	—	+	—	+	+
Sulphide .	NiS								
Colour of sulphide	black								
Catalytic Efficiency	+								

The most active cupric sulphide cupric sulphate catalysts convert *β*-butylene (high boiling form), isobutylene and various mixtures of these compounds with other hydrocarbons, into olefines boiling from about 100-200° C. The figures in Table III show the experimental conditions and the catalytic efficiency.

TABLE II.—DIMERISATION OF TRIMETHYLETHYLENE.

No.	1.	2.	3.	4.
Catalyst ; [Ratio C ₃ H ₁₀ : Catalyst = 7 : 1]	CuS prepared from CuSO ₄ and Na ₂ S	CuS, same sample as No. 1 + 20 per cent. S	CuS, same sample as No. 1 + 20 per cent. CuSO ₄ . 5H ₂ O	CuS prepared from CuSO ₄ and H ₂ S in acid solution and exposed to air until 30 per cent. is converted into CuSO ₄
Per cent. Dimerisation after 60-64 hours	about 3	11	41	70

Experiments 1-15 were done at constant volume under similar conditions to those of Table II. In case 3 it was found that the initial activity of the catalyst did not decrease during the reaction. Experiments 16 and 17 were carried out at constant pressure of about 1 atmosphere by using a flowing method; the through-put was 100-200 l./hour/l. catalyst; the initial activity of the catalyst decreased during the reaction. Under the conditions of Nos. 1-6 the cupric sulphide cupric sulphate catalysts are more efficient in the case of *isobutylene* and trimethylethylene than in

TABLE III.—POLYMERISATION OF OLEFINS.

No.	Starting Substance.	Ratio of Starting Substances.	Time (hours).	Temp. (°C.)	Per Cent. Polymerisation.
1	Sym. Methylenelethylene .	—	64	160	< 3
2	Trimethylenelethylene . . .	—	60	150	23 *
3	β -Butylene	—	63	160	6
4	Isobutylene	—	60	150	45
5	Propylene	—	64	150	< 3
6	Butadiene	—	65	100	< 3
7	Trimethylenelethylene-Pentane .	1 : 3	65	100	11
8	Trimethylenelethylene-sym. Methylenelethylene . .	1 : 3	63	160	12
9	Trimethylenelethylene- β -Butylene .	1 : 3	65	100	24
10	Trimethylenelethylene-Propylene .	1 : 3	64	150	11
11	Trimethylenelethylene-Butadiene .	1 : 3	65	100	8
12	Isobutylene-Pentane	1 : 3	66	150	10
13	Isobutylene-sym. Methylenelethylene	1 : 3	64	150	21
14	Isobutylene- β -Butylene	1 : 3	64	150	37
15	Isobutylene-Propylene	1 : 3	65	150	12
16	β -Butylene	—	4	190	10
17	Isobutylene-Butadiene- β -Butylene- α -Butylene-Isobutane- <i>n</i> -Butane	29 : 19 : 16 : 25 : 4 : 7	5	150-250	10-20

* The catalyst used was not the same as that in No. 4 of Table II.

that of β -butylene, sym. methylenelethylene and butadiene. The polymerisation of butadiene was also investigated at 150° C. but no measurable catalysis could be observed. Trimethylenelethylene and isobutylene are probably selectively polymerised in experiments 7, 8, 10, 11, 12, 13 and 15, but some mixed polymerisation seems to take place in Nos. 9 and 14. It should, however, be possible to carry out a selective polymerisation of isobutylene, also in the presence of β -butylene if pressure and temperature are suitably adjusted.

The mechanism of the catalytic reactions of the Tables I and II and of Nos. 1-15 of Table III is unknown, but for the catalysis under the conditions of experiments 16 and 17 a hypothesis, based on the following observations, can be suggested. A part of the starting substance is converted into carbon dioxide and water, while the copper sulphate is reduced to sulphur dioxide and metallic copper or cuprous oxide. It is therefore possible that the catalysis is connected with an oxydation reduction process in which a peroxidic intermediate compound takes part.

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University College, London.*

DIMERISATION REACTIONS OF UNSATURATED HYDROCARBONS.

BY ERNST BERGMANN.

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In the classical organic chemistry one was accustomed to formulate dimerisation products of unsaturated compounds either as cyclobutane derivatives (A) or even as association products not to be represented by means of a valency scheme. (A) $\begin{array}{c} \text{C}=\text{C} \\ + \\ \text{C}=\text{C} \end{array} \rightarrow \begin{array}{c} \text{C}-\text{C} \\ | \quad | \\ \text{C}-\text{C} \end{array}$ The crystalline dimeride (m.p. 113°) of assym. diphenylethylene ($\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$, e.g., has been assumed by Hildebrand^{1, 2} to be an association product—which assumption was based on the easy desaggregation of the dimeride—and by Staudinger³ to be a tetraphenyl-cyclobutane. The former assumption, evidently, does not convey anything to the chemist, the latter had to be proved experimentally before being accepted, in view of the rareness of cyclobutane compounds in general.^{3a}

Due to the steadily increasing interest in the chemistry of polymerisation reactions, much work has been dedicated lately to the elucidation of their elementary act, the dimerisation, and one may formulate the results of this work as follows: There exist two types of dimerisation reaction: "dimerisation proper" with formation of cyclobutane derivatives, caused exclusively by irradiation, and "migratory dimerisation," with formation of a new olefin, caused by migration of an hydrogen atom (B). Obviously, only type (B) can be regarded as elementary act of a polymerisation; in certain cases the dimerides so formed are apt to undergo secondary isomerisation reactions, with formation of saturated cyclic compounds, which is interesting as chain-breaking mechanism in the polymerisation process.

On the following pages a short review on the experimental data available is given.

Type (B).

(1) **Mono-olefins.**—The activability of a hydrogen atom will naturally depend on the nature of substituents present and on their distribution on both sides of the double bond. Styrene and α -methylstyrene are easily dimerised, β -methylstyrene⁴ not. In the same way, these factors will govern the degree of polymerisation reached, by determining the activability of the hydrogen atom apt to migrate in the olefinic dimeride.

¹ Hildebrand, *Dissertation*, Strassburg, 1909.

² Compare Schroeter's assumptions on the structure of the ketene dimerides (see below); *Ber.*, 1916, 49, 2967; *Z. angew. Chem.*, 1911, 24, 231.

³ Staudinger and Kon, *Annalen*, 1911, 384, 85.

^{3a} The formula of 1,2-dimethylene-cyclobutane, suggested by Lebedew (*Chem. Centralblatt*, 1914, 1, 1410) for the dimeric allene, is still less probable.

⁴ The product obtained by Errera (*Gazz. Chim. Ital.*, 1884, 14, 509) through reaction of sodium is chemically not defined.

Besides these internal factors, a number of external ones will obviously play an important part: nature of the catalyst, solvent, temperature, pressure—in some cases extensively studied by Staudinger and his co-workers.⁵ But it remains still impossible to formulate definite rules. Butylene, *e.g.*, can easily be converted into high-molecular polymerides,⁶ but neither the dimeride of 1-, nor of one of the two stereoisomeric 2-butenes can easily be prepared. Only recently Ipatieff⁷ has reported that the butylenes are to a certain extent dimerised at high pressure and high temperature in the catalytic presence of phosphoric acid; the structure of the dimeride, however, has not been elucidated. On the other hand, isobutylene⁸ can easily be dimerised and converted into other low-molecular polymerides.

Evidently, assymetrical substitution favours dimerisation (and polymerisation) reactions. This is marked in the series of aryl-olefins, which is more extensively studied than purely aliphatic unsaturated compounds. Styrene,⁹ α -methylstyrene¹⁰ and α -phenylstyrene^{11, 12} (assym. diphenylethylene) give easily—according to scheme (B), well-defined dimerisation products, and the same is true for indene¹³ which may be regarded as a styrene derivative, but as a β -substituted one, so its easy dimerisation is somewhat surprising. One may assume that the assymetry induced by a phenyl and a benzyl group, respectively, on both sides of the double bond is great enough to permit hydrogen migration (indol and skatol behave exactly like indene).^{13a} The same reasoning applies to certain nuclear substitution products of β -methylstyrene, which in contrast with β -methylstyrene itself are very easily dimerised, *e.g.*, anethol¹⁴ or isoeugenol, which are as easily dimerised as *p*-isopropenyl-anisol,¹⁵ *p*-isopropenylaniline,¹⁶ etc. Halogen atoms, on the other hand, seem to decrease the polymerisability; *p*, *p'*-dichlorodiphenylethylene, *e.g.*, could not be polymerised by Schreiber^{16a} and even the corresponding mono-bromo-compound proved stable, in the recent experiments of Schmitz-Dumont, Thoemke and Diebold.¹⁷

p, *p'*-Dimethoxy-diphenylethylene was also found to be resistant against the attack of polymerising agents,^{16a, 17} but the influence of the

⁵ Compare Staudinger's comprehensive treatise *Die hochmolekularen organischen Verbindungen* (J. Springer, Berlin, 1932).

⁶ Weizmann and Legg, *Chem. Centralblatt*, 1922, II, 1218; IV, 711.

⁷ Ipatieff, *Catalytic reactions at high pressures and temperatures*, p. 628 (Macmillans Company, New York, 1936).

⁸ Butlerow, *Annalen*, 1876, 180, 247; 1877, 189, 46. Structure of the dimeride, Whitmore and Church, *J. Amer. Chem. Soc.*, 1932, 54, 3710.

⁹ Fittig and Erdmann, *Annalen*, 1883, 216, 179. Stobbe and Posnjak, *ibid.*, 1909, 371, 287.

¹⁰ Staudinger and Breusch, *Ber.*, 1929, 62, 442. Bergmann, Taubadel and Weiss, *Ber.*, 1931, 64, 1483.

¹¹ Lebedew *et al.*, *Ber.*, 1923, 56, 2349. Bergmann and Weiss, *Annalen*, 1930, 480, 49. Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, 52, 4021.

¹² For the polymerisation of similar compounds, see Schoepfle and Ryan, *l.c.*¹¹

¹³ Bergmann and Taubadel, *Ber.*, 1934, 65, 463. Compare also Whitby and Katz, *Chem. Centralblatt*, 1932, 1, 386; *J. Amer. Chem. Soc.*, 1928, 50, 1160. For 3-phenyl-indene, see Marvel and Pacevitz, *ibid.*, 1938, 60, 2816.

^{13a} Schmitz-Dumont, *Annalen*, 1934, 514, 267.

¹⁴ Staudinger, *Helv. chim. acta*, 1929, 12, 972, 983. Compare Beilstein, Vol. VI, p. 568 (Berlin, J. Springer, 1923).

¹⁵ Behal and Tiffeneau, *Bl. Soc. chim. France*, 1908, (4) 3, 320. J. v. Braun, *Annalen*, 1929, 472, 66.

¹⁶ J. v. Braun, *ibid.*, 13, 40.

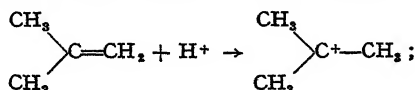
^{16a} Schreiber, *Dissertation*, Berlin, 1933.

¹⁷ Schmitz-Dumont, Thoemke and Diebold, *Ber.*, 1937, 70, 575.

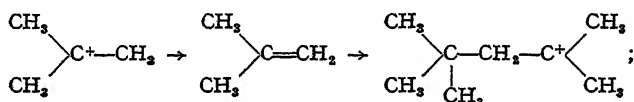
p-methoxy groups is neutralised by halogens, *e.g.*, *m*-bromo-atoms; *p*, *p'*-dimethoxy-*m*, *m'*-dibromo-diphenylethylene polymerises^{17a} as well as *p*-methoxy-*p'*-chloro-diphenylethylene.^{17b}

A similar influence of the degree of asymmetry on the course of addition reactions has been observed for the alkali metal addition to arylated olefins¹⁸ and for that of phosphorus pentachloride^{18a} (as $\text{PCl}_5 + \text{Cl}$), while the "classical" addition reaction, *viz.*, that of bromine follows quite a different course: increasing methylation of ethylene increases regularly the capability of the double bond to combine with bromine.¹⁹ There can be no doubt that this difference is due to the different mechanism of the addition in the two groups of cases: the asymmetry is important for atomic addition reactions.²⁰

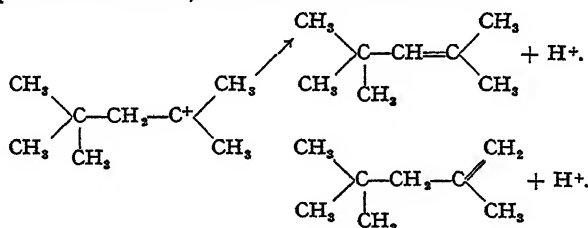
Whitmore²¹ has recently suggested a mechanism for dimerisation which involves the primary addition of a proton, *e.g.*,



the positive carbonium ion formed adds, exactly like the proton, to a second molecule of isobutylene:



finally a proton is released, and a double bond formed:



As in most cases the dimerising agent is acid, this theory is quite impressive; but it may be remembered that in certain cases, dimerisation may take place in absence of a proton. So it has been stated by Schoepfle and Ryan²² that the formation of the unsaturated dimeride from assym. diphenylethylene takes place in presence of stannic chloride, while in presence of stannic chloride plus hydrochloric acid the saturated dimeride is formed, and under the influence of sodium-powder, α -methyl-

^{17a} The polymerisation products of eugenol and safrol, which are benzyl-ethylene derivatives, have not been studied from the point of view of chemical structure. Whitby and Katz, *Chem. Centralbl.*, 1932, I, 387. With regard to *p*-allyl phenol, see van der Zanden, *Rec.*, 1938, 57, 233; 1939, 58, 181.

^{17b} For the influence of substituents on the polymerisation of ω -nitro-styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}\cdot\text{NO}_2$, see *J. Amer. Chem. Soc.*, 1938, 60, 2841.

¹⁸ Schlenk and Bergmann, *Annalen*, 1930, 479, 42.

^{18a} Bergmann and Bondi, *Ber.*, 1931, 64, 1455.

¹⁹ Ingold and co-workers, *J. Chem. Soc.*, 1931, 2354; 1935, 984; 1936. Compare also Schlenk and Bergmann, *l.c.*; Bergmann and v. Christiani, *Ber.*, 1930, 63, 2559.

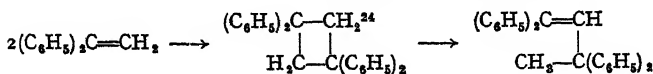
²⁰ Compare Bergmann, *Helv. chim. acta*, 1937, 20, 590.

²¹ Whitmore, *Ind. Eng. Chem.*, 1934, 26, 94.

²² Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, 52, 4021.

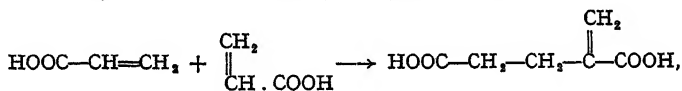
styrene suffers first dimerisation, before the sodium addition starts.²³ The dimerising action of molecular iodine too—*e.g.*, in the case of assym. diphenylethylene¹—cannot be explained in terms of this theory. Moreover, the kinetic properties of such dimerisation reactions, as studied by Schmitz-Dumont,^{23a} are not in accordance with this mechanism; they fit better into the scheme of a reaction between two molecules activated under the influence of the catalyst. Perhaps, both mechanisms, transference of a hydrogen atom and the successive addition of a proton and a carbonium ion, may actually occur.

Schoepfle and Ryan²² discuss the possibility that assym. diphenylethylene dimerises primarily into a cyclobutane derivative which isomerises into the actually isolated unsaturated dimeride:

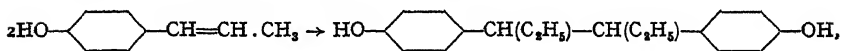


but there is no experimental evidence to support this mechanism, and in many cases it may well be doubted that a cyclobutan derivative of this type is easily isomerised—the photo-dimeride of stilbene, *e.g.*, which is regarded as 1.2.3.4-tetraphenyl-cyclobutane (see below) seems quite stable.

All these catalytic dimerisations proceed so as to convert methylene groups into methyls and methine into methylene groups. Thereby, they are differentiated from other dimerisation reactions, which most probably follow a much less simple course. Sodium ethylate, *e.g.*, converts acrylic acid into α -methylene-glutaric acid:^{24a}



and crotonic acid behaves analogously.²⁵ This difference is certainly not due to the presence of the carboxyl group, as β -methyl-crotonic acid, under the influence of aluminium chloride, dimerises according to scheme (B),²⁶ but rather to the presence of alkali; in fact it has recently²⁷ been observed, that the alkaline dimerisation of the (carboxyl-free) anethol leads to 3.4-di-(*p*-hydroxyphenyl)-hexane



the additional hydrogen being supplied from unknown sources.

But even under the favourable conditions of a dimerisation by means of acid or halogenides of the aluminium or stannic chloride type, there exist some exceptions from the above generalisations, which therefore have to be discussed. We may exclude from this discussion processes secondary to the dimerisation reaction proper, *e.g.*, cyclisation (in the arylated series) or migration of the double bond in the olefine formed, as take place in the case of α -methylstyrene, assym. diphenylethylene,

²³ Bergmann and Weiss, *Ber.*, 1931, 64, 1497.

^{23a} Schmitz-Dumont, *ibid.*, 1938, 71, 205.

²⁴ The axial-symmetric structure is impossible, as apparently 1.1.2.2-tetraphenylcyclobutane does not exist.

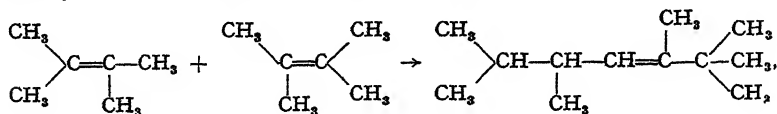
^{24a} Pechmann and Roehm, *Ber.*, 1901, 34, 427.

²⁵ Pechmann, *ibid.*, 1900, 33, 3323.

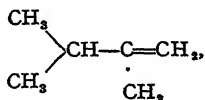
²⁶ Bergmann and Weiss, *ibid.*, 1931, 64, 1496.

²⁷ Dodds and Robinson, *Nature*, 1938, 142, 1121.

triphenyllene²⁸ or in that of styrene.²⁹ The dimerisation of tetramethylethylene can obviously not follow mechanism (B) and even the mechanism suggested by Whitmore can only explain the structure of the dimeride, recently elucidated by Brunner and Farmer³⁰:



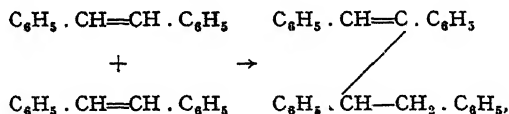
if one allows for migration of a methyl group. The hydrogen atoms transferred derive from one of the methyl groups; so as the dimerising form of tetramethyllallene we may take its allylic isomer



which fits better into the possibilities of scheme (B).

One may safely assume that the analogously surprising polymerisability of tetramethyllallene³¹ is to be explained on the same lines.

Another anomalous case of dimerisation is that of stilbene, observed by Wieland and Dorrer,³² under the influence of aluminium chloride. It is surprising that this symmetrical compound dimerises at all, and the structure of the dimeride is neither in accordance with scheme (B), leading to 1.2.3.4-tetraphenyl-butene-(1), the dimerisation product being resistant towards bromine,



nor may it be explained by allylic isomerisation or cyclisation of such a product into sym. diphenyl-dibenzyl-ethylene,³³ 1.2-diphenyl-3-benzyl-hydrindene,³⁴ 1.2.3-triphenyl-1.2.3.4-tetrahydronaphthalene³⁵ or similar products.^{35a} It seems possible, that the dimerisation is preceded by an assymetrisation of the molecule, which would be inverse to the well-known transformation of assym. diphenylethylene

²⁸ Ziegler and Ochs, *Ber.*, 1922, **55**, 2257. Ziegler, Grabbe and Ultrich, *ibid.*, 1924, **57**, 1983. Straus and Ehrenstein, *Annalen*, 1925, **442**, 93.

²⁹ Isomerisation of 1.3-diphenyl-butene-(1) into 1.3-diphenyl-butene-(2): Stoermer and Kootz, *Ber.*, 1928, **61**, 2330. According to Risi and Garvin (*Canadian J. Res. Sect. B.*, 1936, **14**, 255), however, the isomerisation involves cyclisation (to 1-phenyl-3-methyl-hydrindene) here, too.

³⁰ Brunner and Farmer, *J. Chem. Soc.*, 1937, 1039.

³¹ Mereshkowski, *Chem. Zentralblatt*, 1914, **1**, 1815; Gapon, *ibid.*, 1932, **II**, 2167. For the relations to the allyl-isomeric 2.4-dimethyl-pentadiene-(1.3), see Slobodin, *ibid.*, 1937, **I**, 4491.

³² Wieland and Dorrer, *Ber.*, 1930, **63**, 404.

³³ Described by Bergmann, Winter and Schreiber, *Annalen*, 1933, **500**, 122.

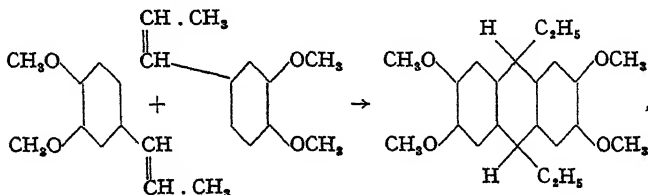
³⁴ Described by Bergmann and Weiss, *ibid.*, 1930, **480**, 64; Bergmann and Schreiber, *ibid.*, 1933, **500**, 118; compare ³³.

³⁵ Described by Bergmann and Zwecker, *ibid.*, 1931, **487**, 155.

^{35a} For a detailed discussion of the problem, see Schreiber, *Thesis*, Berlin, 1933.

derivatives into those of the symmetrically substituted stilbene,³⁶ but even for this mechanism no experimental proof is available so far.^{35a}

For the dimerisation product of isoeugenol methyl ether, Haworth and Mavin^{36a} have suggested the formula of 9.10-diethyl-9.10-dihydro-2.3.6.7-tetramethoxy-anthracene, as chromic oxidation gave small amounts of the corresponding quinone

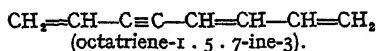


and an analogous structure was advocated by Robinson^{36b} for the dimeride of isosafrol. It has, however, reported^{36c} recently bromination experiments which cast doubt upon this formulation, and prefer rather a cyclobutanic structure. The problem seems still unsettled; but it may be pointed out that the available data would fit into the usual scheme of hydrindene formation too.

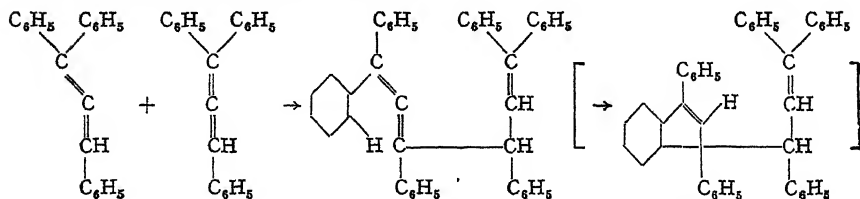
(2) **Acetylenes.**—The dimerisation of acetylenes seems to follow completely scheme (B). It is well-known that acetylene itself is dimerised into vinylacetylene.³⁷



and the dimerisation of this substance gives a C_8 -hydrocarbon of the following structure:³⁸



(3) **Allenes.**—The same is true for the one case of the dimerisation of an allene, in which the structure of the reaction product is known. Triphenylallene³⁹ dimerises according to the following scheme, but the dimerisation proper is followed by the characteristic cycloisomerisation of arylated allene derivatives:



³⁶ Hepp, *Ber.*, 1874, 7, 1409. Quelet and Allard, *Bull. Soc. chim. France*, (5), 1938, 5, 1273. Compare also Schlenk and Bergmann, *Annalen*, 1928, 463, 75. Wooster and Mitchell, *J. Amer. Chem. Soc.*, 1930, 52, 1043; Wooster and Ryan, *ibid.*, 1932, 54, 2419.

^{36a} Haworth and Mavin, *J. Chem. Soc.*, 1931, 1363.

^{36b} Robinson, *ibid.*, 1915, 107, 267.

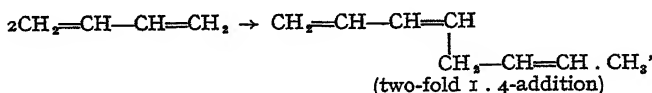
^{36c} Haraszi and Szeki, *Annalen*, 1933, 503, 294. Compare Puxeddu, *Chem. Centralbl.*, 1934, II, 934.

³⁷ Nieuwland, *et al.*, *J. Amer. Chem. Soc.*, 1931, 53, 4197, and later publications.

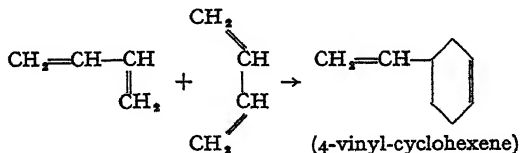
³⁸ Nieuwland, Calcott, Downing and Carter, *ibid.* Dykstra, *ibid.*, 1934, 56, 1625. The cyclobutanic structure of a second dimeride of vinylacetylene, suggested in the latter paper, seems unfounded.

³⁹ See note 28.

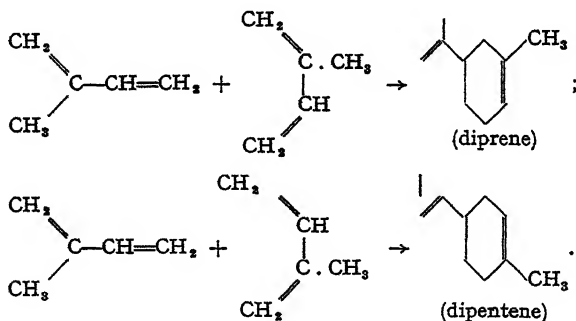
(4) **Dienes.**—The dimerisation of conjugated unsaturated hydrocarbons gave—in all those cases, where the structure of the dimeride has been elucidated—products which do not directly correspond to scheme (B). This scheme would obviously lead to an open-chain dimeride with three double-bonds, *e.g.*,



while actually a doubly-unsaturated cyclic hydrocarbon is obtained. In the case of butadiene⁴⁰ and isoprene⁴¹ its structure is formally explained by the assumption that one diene molecule in 1.2 adds to the second one in 1.4, *e.g.*,



In the case of isoprene, the less substituted double bond is the point of the 1.2-attack, while the second molecule adds according to the two theoretically expected schemes :



2. 3-Dimethyl-butadiene behaves analogously,⁴² myrcene^{42a} gives camphorene, mixed dimerisation of aliphatic butadienes⁴³ follows the same course ; and so does the well-studied polymerisation of cyclopentadiene^{43a} and cyclohexadiene.^{43b} Naturally, the isolation of these cyclic dimerides does not exclude that they are formed in two successive steps, by dimerisation according to scheme (B) and subsequent cycloisomerisation. As a matter of fact, the isolation of the open-chain C₁₀ alcohol geraniol from the dimerisation of isoprene under hydrating conditions by Wagner-Jauregg⁴⁴ shows at least that dimerisation of a diene *may* give an open-chain compound. The dimerisation of 1-phenylbutadiene finally, is

⁴⁰ F. Hofmann, *Z. angew. Chem.*, 1912, 25, 1465. Alder and Rickert, *Ber.*, 1938, 71, 373.

⁴¹ Wagner-Jauregg, *Annalen*, 1931, 488, 176.

⁴² Farmer and Pickethly, *J. Chem. Soc.*, 1938, 11.

^{42a} Semmler and Jonas, *Ber.*, 1913, 46, 1569.

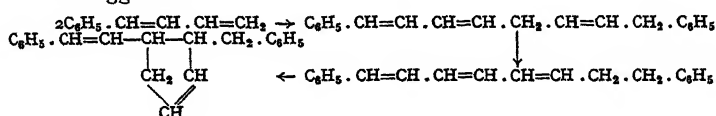
^{43a} Alder and Stein, *Annalen*, 1931, 485, 223.

^{43b} *Ibid.*, 1932, 496, 197.

⁴⁴ Wagner-Jauregg, *ibid.*, 1932, 496, 52.

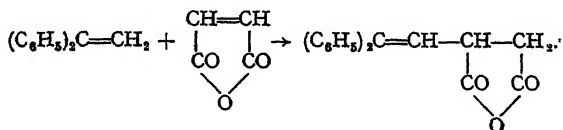
⁴³ *Ibid.*, 1914, 47, 2077.

most easily understood on the basis of a two-step reaction. The product, namely, is not a cyclohexene, but, as recently shown,⁴⁵ a cyclopentene derivative (2-benzyl-1-styryl- Δ^3 -cyclopentene). The following scheme has been suggested:



But Farmer and Pitkethly⁴⁶ are of the opinion, that even this system may be formed without intermediates. Unfortunately, in other cases, where well-defined dimerides of substituted dienes have been isolated, their structure has not yet been elucidated, *e.g.*, for 1-phenyl-3-methyl- and for 1,3-diphenyl-butadiene-(1,3). Extensive investigations, however, have been carried out with regard to the influence of number and position of substituents (methyl and phenyl groups) on the polymerisability of the diene system,⁴⁷ which again show the dominating rôle of the unsymmetry conferred upon the molecule by the substituents: of the isomeric dimethylbutadienes the 2,3-compound has the highest, the 1,4-compound the lowest polymerisation rate; 1-phenyl- and 1-phenyl-3-methyl-butadiene polymerise more easily than butadiene and 3-methyl-butadiene (isoprene); 1,1,4,4-tetramethyl- and tetraphenyl-butadiene are not polymerised at all, etc. This regularity may perhaps be taken as another argument in favour of the assumption, that diene dimerisation proceeds via an open-chain dimeride according to scheme (B)—which subsequently suffers cycloisomerisation. In the case of dienes again, secondary reactions may occur, as has been shown for 2,3-dimethyl-butadiene by Farmer and Pitkethly⁴² (formation of a dicyclic dimeride from the monocyclic primary product).

(5) Concluding Remarks.—In this connection, it is interesting that the migratory dimerisation has some parallels in the migrating additions of hydrocarbons to unsaturated systems, which—following a notion suggested by Wagner-Jauregg⁴⁸—may be classified as “migratory hetero-dimerisation.” Maleic anhydride, *e.g.*, reacts with assym. diphenylethylene in the first stage according to the following scheme^{49, 50}:



The product formed reacts, subsequently, with another molecule of the anhydride. The nuclear hydrogen atoms of pyrrol⁵¹ and similar heterocyclic systems⁵² combine with maleic anhydride exactly in the same way.

The addition of benzene (as $\text{C}_6\text{H}_5 + \text{H}$) or its derivatives and homologues to certain unsaturated systems, finally, is obviously of an analogous

⁴⁵ Bergmann, *J. Chem. Soc.*, 1935, 1359.

⁴⁶ Farmer and Pitkethly, *ibid.*, 1938, 11.

⁴⁷ Whitby and Gallay, *Chem. Centralblatt*, 1932, II, 1425.

⁴⁸ Wagner-Jauregg, *Ber.*, 1930, 63, 3213.

⁴⁹ Wagner-Jauregg, *Annalen*, 1931, 491, 1.

⁵⁰ Compare Rosenthal, *Dissertation*, Berlin, 1932.

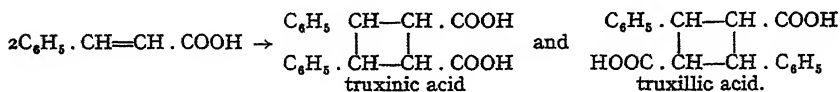
⁵¹ Diels and Alder, *Annalen*, 1931, 486, 211; 1931, 490, 267.

⁵² *Ibid.*, 1931, 490, 277; 1932, 498, 1.

character. Under the influence of catalysts (concd. sulphuric acid or aluminium chloride), ethylenes react more or less easily.^{52a} The reaction is smoother, when the reaction partner is highly reactive, as acetylene⁵³ or the strongly polar α , β -unsaturated carbonyl and carboxyl compounds.⁵⁴

Type A.

It has been pointed out already that the dimerising formation of cyclobutane compounds from olefines takes place only under the influence of ultraviolet light. For the dimerisation of cinnamic acid, the structure of the compounds formed has been proved experimentally by Stoermer and co-workers,⁵⁵ and it is reasonable to assume that the similarly constituted ketones of the dibenzalacetone type⁵⁶ behave correspondingly.



For hydrocarbons, the analogous proof has never been put forward, so the assumption that the dimeric stilbene⁵⁷ is tetraphenylcyclobutane, is actually unfounded. But in favour of our general thesis the behaviour of anthracene may be quoted. This dimerises photochemically—in absence of air—to give the so-called para-anthracene,⁵⁸ which evidently consists of two dihydro-anthracene systems, arranged in two parallel planes and held together by 9.10-valencies. It is interesting to note the influence of meso-substituents⁵⁹ on the photodimerisation of anthracene: 9-Bromo-, 9-carboxy-, 9-methyl and 9-ethyl-anthracene behave like anthracene, while 9.10-dimethyl- and 9-methyl-10-ethyl-anthracene are not affected by irradiation.⁶⁰

One case, which seems to contradict the above rule, is that of the non-photochemical dimerisation of ketenes. The products were invariably formulated as cyclobutanediones,^{60a} but no proof whatever has been put forward to support this formula. On the contrary, Hurd and Williams⁶¹ have proved that the dimeric ketene itself is not cyclobutanedione-(1,3),⁶² but acetyl-ketene. Naturally, an analogous mechanism of

^{52a} See, e.g., Kraemer and Spilker, *Ber.*, 1890, **23**, 3169, 3269; 1891, **24**, 2785. Brochet, *Compt. rend.*, 1893, **117**, 115. Compare Ipatieff, *Catalytic reactions at high pressures and temperatures*, pp. 651 ff. (Macmillan Company, New York, 1936).

⁵³ Berthelot, *Bl. Soc. chim. France*, (2), 1886, **6**, 279.

⁵⁴ See e.g., Liebermann and Hartmann, *Ber.*, 1891, **24**, 2582; 1892, **25**, 957. Kohler, *Amer. Chem. J.*, 1904, **31**, 642. Eijkman, *Chem. Centralbl.*, 1907, **II**, 2045; 1908, **II**, 1100.

⁵⁵ See e.g., Stoermer and Bacher, *Ber.*, 1922, **55**, 1861, 1869; and as the last papers of this series: Stoermer and Starck, *ibid.*, 1937, **70**, 479; Stoermer, Starck and Anker, *ibid.*, 1937, **70**, 483.

⁵⁶ E.g., dibenzalacetone: Praetorius and Korn, *ibid.*, 1910, **43**, 2744. Cinnamylidene-acetophenone: Stobbe, *ibid.*, 1911, **44**, 869, 960. Cinnamal-acetone: Stobbe, Hensel and Simon, *J. pr. Chem.*, (2), 1928, **110**, 129, etc.

⁵⁷ Ciamician and Silber, *Ber.*, 1902, **35**, 4129.

⁵⁸ See the comprehensive treatise of Bacher in *Abderhalden, Handbuch der biologischen Arbeitsmethoden*, Section I, Part 2/II, pp. 1462 ff.

⁵⁹ For the influence of substituents in the other nuclei, see Bacher, *l.c.*

⁶⁰ Willemart, *Compt. rend.*, 1937, **205**, 993.

^{60a} Staudinger, *Die Ketene*, p. 38 (Stuttgart, F. Enke, 1912).

⁶¹ Hurd and Williams, *J. Amer. Chem. Soc.*, 1936, **58**, 962.

⁶² The physical arguments put forward by Angus, Leckie, Le Fèvre, Le Fèvre and Wassermann (*J. Chem. Soc.*, 1935, 1751) are obviously insufficient.

dimerisation cannot apply to disubstituted ketenes.⁶³ The spectra of the dimeric ketenes⁶⁴ which have been quoted in favour of the cyclobutane formulæ, show nothing more than the presence of carbonyl groups in the dimerisation products, the bands being somewhat shifted from the usual wave-lengths, but they are unable to supply a definite proof of the cyclobutanic structure. The problem, apparently, remains open.

Finally, a word may be said on the "heterodimerisation" between ketenes and olefins. This reaction, occurring without the influence of light does yield cyclobutane derivatives, as has been shown for the pairs: diphenylketene + cyclopentadiene,^{65, 67, 68} styrene,⁶⁶ cyclohexene,⁶⁷ cyclohexadiene⁶⁷ and cyclopentene.⁶⁷

Summary.

Dimerisation of olefins yields cyclobutane derivatives only when the agent is light. "Catalytic" dimerisation of olefins proceeds generally by migration of a hydrogen atom. The experimental evidence in favour of these two rules is presented; and some (apparent or real) exceptions are quoted and discussed.

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⁶³ The "dimeric diphenylketen" of Langenbeck (*Ber.*, 1928, 61, 938; compare Wittig, *ibid.*, 1928, 61, 1627, is not actually a dimerisation product of diphenylketen as it is not formed from the latter one in isolated form. Suggestions about its structure: Bergmann, *J. Chem. Soc.*, 1938, 727.

⁶⁴ Lardy, *Dissertation Zürich*, 1923 (Paris, Les Presses Universitaires de France).

⁶⁵ Lewis, Ramage, Simonsen, and Wainwright, *J. Chem. Soc.*, 1937, 1837.

⁶⁶ Bergmann, *J. Chem. Soc.*, 1938, 727.

⁶⁷ Farmer, *Chem. Ind.*, 1937, 56, 1080; Farmer and Farooq, *J. Chem. Soc.*, 1938, 1925.

⁶⁸ Smith, Agre, Leekley, and Prichard, *J. Amer. Chem. Soc.*, 1939, 61, 7.

LOW-MOLECULAR POLYMERISATION OF DIENES AND TRIENES.

BY ERNEST HAROLD FARMER.

Received 2nd February, 1939.

When mono-, di- and poly-olefines are polymerised the products may be linear polymers of considerable molecular weight belonging to a polymer-homologous series, or they may form a low-molecular series comprising such early polymers as dimer, trimer, etc., but rarely going in substantial yield beyond hexameric complexity. The nature of the low-molecular series which actually turns up in any case depends on the structure and physical state of the unsaturated hydrocarbon, the nature of the catalyst or polymerising agency, and the experimental conditions: in some instances the dimeride alone may appear, in others the lowest polymer to be isolated may be the trimer, tetramer, etc., but very frequently a short series containing the dimer and its immediate successors is formed.

The structure of the low-molecular polymers differs greatly from that of the characteristic linear polymers in which the monomeric units are linked end to end, except perhaps among the dimers of mono-olefines, where discrimination may not be possible. Extensive branching of the chain occurs among the dimers, trimers, etc., of mono-olefines, and cyclisation among the polymers of di- and tri-olefines. In view of the structural diversity characterising the low-molecular products which have been reported as arising from mono-olefines, and of the very different experimental means which have been employed to effect polymerisation in the various examples, it would be unsafe to assume that one general reaction-mechanism can cover all cases; indeed it would seem that there is much experimental work to be done before the polymeric structures can adequately be correlated with specific reaction-mechanisms.

The present account is concerned with the types of structures which are formed by low-molecular polymerisation of conjugated and unconjugated dienes and trienes. Up to the present, the production of low-molecular polymers of linear type from conjugated di- and tri-olefines has not been reported,* but there is no difficulty in obtaining non-linear dimeric, trimeric, etc., polymers from all the simple conjugated dienes. The nature of a number of low-molecular series which are thus obtainable, and the structure of certain individual polymers are described below. Over the past few years various suggestions as to the reaction mechanisms concerned in low-molecular additions have been made, these including hypotheses involving proton-addition, catalyst-addition, the production of rather indefinitely-specified olefinic activations or of active free-radical forms; but so far as the general course of reaction is concerned the mechanisms mostly rest, save where free-radical intermediates are postulated, on a polar basis. The possibility of accounting on a polar basis for the various polymeric structures here dealt with is considered.

Polymerisation of Conjugated Dienes.

Number of Cyclohexenic Forms.—All save one of the conjugated diene hydrocarbons whose dimerising tendencies have been examined up to the present yield *cyclohexenic* dimeric forms; α -phenylbutadiene alone has been shown to give a *cyclopentenic* dimeride. Now any unsymmetrical conjugated diene such as isoprene or piperylene is composed of two dissimilarly substituted ethylene units, and these units have presumably somewhat different polarising tendencies. It is of interest, therefore, to enquire whether all the four *cyclohexenic* dimerides which the combination of two molecules of the diene on the Diels-Alder plan in all the possible ways should generate are actually formed in practice, or whether on the contrary the differences in the polarising tendencies of the units can be sufficient to suppress some of the forms.

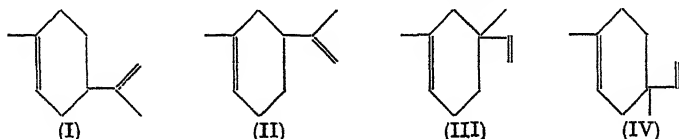
The fullest evidence available refers to thermally-polymerised isoprene, where the work of several authors shows unquestionably that the

* Excluding the alleged formation of β -myrcene from isoprene,¹ and also the frequently-cited formation of dihydro-dimerides of isoprene by reduction with sodium and alcohol,² in which the mechanism of reaction, like that involved in the formation of other bimolecular reduction products, is probably quite distinct from the polymeric mechanism.

¹ Ostromysslenski and Koschelev, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 1928 *J. Soc. Chem. Ind.*, 1916, 35, 368.

² Midgley, Henne, and Leicester, *J. Amer. Chem. Soc.*, 1936, 58, 1961.

menthadienes (I) and (II) are formed,³ whilst the work of Lebedev and Merezhkovski⁴ shows pretty clearly that a third form also is present, and

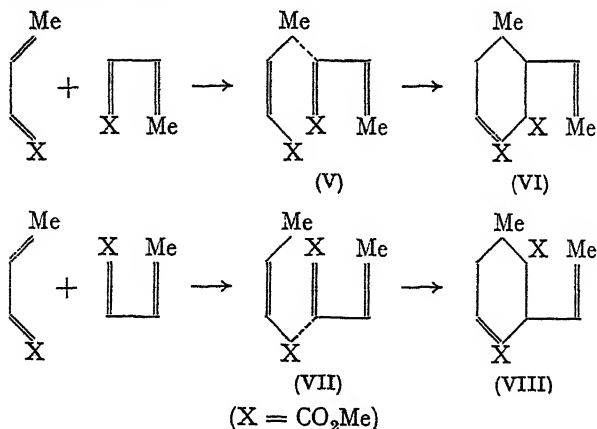


this form on the evidence supplied could be either (III) or (IV).

The Linking of Molecules.—It will be generally conceded that some sort of open-chain dimeric structure is formed transiently as a preliminary to the cyclic structure, or in other words that one of the bonds linking the monomers is formed before the other. Robinson⁵ pictured the Diels-Alder reaction between a diene and maleic anhydride as resulting from the anionoid reactivity of the diene in conjunction with the normal kationoid reactivity of the $\text{CH}:\text{CH}\cdot\text{CO}$ group of the maleic anhydride.



If dimerisation of isoprene is initiated by a precisely similar polar mechanism, then in order to produce four structurally isomeric dimerides, polarisation of each ethylene unit must be able to occur in either direction. Striking evidence on this point is furnished by recent work on the thermal dimerisation of α -carboxylated dienes.⁶ Sorbic ester when heated at $230\text{--}235^\circ\text{C}$. in a closed vessel yields a mixture of at least three *cyclohexenic* dimerides, of which two are the crystalline forms (VI) and (VIII) and the residue probably



³ Lebedev, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949; 1913, **45**, 1249, 1296; Lebedev and Ivanov, *ibid.*, 1916, **48**, 997; Wallach, *Annalen*, 1885, **227**, 277; Wagner-Jauregg, *ibid.*, 1931, 488, 176.

⁴ Lebedev and Merezhkovski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1379.

⁵ Robinson, *Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions*, 1932.

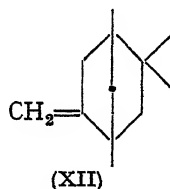
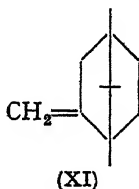
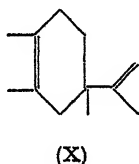
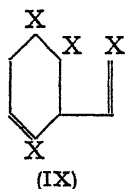
⁶ Farmer and Morrison-Jones, unpublished work.

(although not proved with certainty) stereoisomeric forms of these. It is quite to be anticipated (in view of the ease of maleic anhydride addition to dienes) that the strongly polar $\text{CH}:\text{CH}.\text{CO}$ unit rather than the $\text{CHMe}:\text{CH}.$ unit of one molecule of the conjugated acid will be utilised for addition to the second molecule of acid, but it is of considerable interest that the kationoid influence normally exerted by the carboxyl group on the diene chain of this second molecule appears to be insufficiently exerted, if the polar view is valid, to prevent polarisation of this chain proceeding in the normally unfavoured sense



Assuming that the first bond established between the reacting molecules is that indicated by the dotted lines in (V) and (VII) (*cf.* Robinson's mechanism), it follows that the molecules are capable of becoming ultimately linked *either* by a tail-to-tail or a head-to-tail bond. Whether or not comparable tail-to-tail linkings occur at all in high-molecular polymerisations of the acrylic esters (the usual facile accomplishment of which is presumably largely dependent on the polar influence exerted on the ethylenic unit by the carbonyl group) is not at present known.

The thermal dimer of sorbic ester is accompanied by a trimer, but no appreciable amount of tetramer is formed. It may be mentioned in passing that if carboxyl groups are attached at both ends of the diene chain as in muconic ester, $\text{EtO}_2\text{C}.\text{CH}:\text{CH}.\text{CH}:\text{CH}.\text{CO}_2\text{Et}$, then dimerisation occurs comparably with sorbic acid. Two, or more probably three, dimeric products are formed by heating muconic ester at



175–180° C., one of which is (IX) ($\text{X}=\text{CO}_2\text{Et}$) and the others appear from short examination to be geometrical or double bond isomerides of (IX); also there is a considerable trimeric fraction.⁷ The position of the endocyclic bond, adjacent to a carboxyl group, in the dimerides (VI), (VIII) and (IX) is to be noted.

Thermal and Acid-Catalysed Dimerisation.—Butadiene, 1 : 3- and 1 : 4-dimethylbutadiene⁸ and isoprene⁹ all polymerise, but with different speeds, in an acid medium, and in the case of isoprene, cyclohexenic dimers identical with the corresponding heat-formed dimers (I) and (II) are produced. 2 : 3-Dimethylbutadiene, in an acid medium, likewise gives a Diels-Alder type of dimer (X),⁸ but this is not the only dimer formed : there is a crystalline bicyclic dimer (at least 4 per cent. yield) possessing a methyleno-bicyclohexenic structure whose formula after detailed examination appears most probably to be (XI),¹⁰ although the formulæ (XII) and (XIII) have not been finally excluded; moreover there may well be other structurally distinct or stereoisomeric forms

⁷ Farmer and Ahmad, unpublished work.

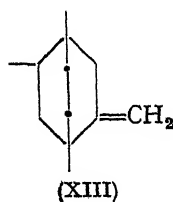
⁸ Farmer and Pitkethly, *J. Chem. Soc.*, 1938, 13.

⁹ Wagner-Jauregg, *Annalen*, 1932, 496, 52.

¹⁰ Farmer and Pitkethly, *J. Chem. Soc.*, 1938, 287.

since the physical properties of the dimeric fraction show it to be highly heterogeneous.*

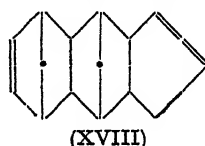
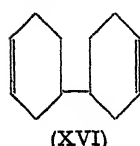
Vaughan¹¹ on rather meagre evidence suggested that thermally dimerised butadiene probably contains bicyclic dimeric material, but Harkness, Kistiakowsky and Mears¹² on very similar evidence concluded



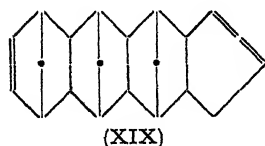
that no appreciable proportion of bicyclic dimeride can be formed. More definite, however, is the oxidative evidence provided by Lebedev⁴ and by Farmer and Pit-

kethly,⁸ which in our view gives very strong indication that two additional bicyclic forms of dimeric dimethylbutadiene (possibly XIV and XV) are present respectively in the thermal and acid-catalysed dimerides.

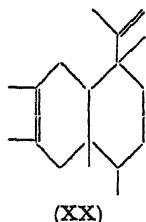
Thermal and Acid-Catalysed Trimerisation.—The extracyclic double bond of the cyclohexenic dimerides seems always to be more re-



active than the endocyclic one. Alder and Rickert¹³ have recently been able to



show that dimeric butadiene (1-vinyl- Δ^3 -cyclohexene) when heated with its monomer in the presence of acetylenedicarboxylic acid (the latter to inhibit polymerisation of the butadiene) adds the monomer in Diels-Alder fashion at the extracyclic bond to give a trimer (XVI). Previously Alder and his collaborators¹⁴ had shown that the double bond in the bridged-ring of dimeric cyclopentadiene (XVII) is the more reactive one of the two, and adds the monomeric structure under the influence of heat to give in turn (XVIII) and (XIX).



Now this Diels-Alder type of thermal trimerisation does not seem to be at all characteristic of acid-catalysed trimerisation and indeed close search has failed to show that even a very small yield of a dimer corresponding to (XVI) is present in acid-catalysed dimeric dimethylbutadiene, although it seems probable that by employing Alder and Rickert's procedure such a trimer might be formed. On the contrary 2:3-dimethylbutadiene yields side by side with its dimers a trimer which recent work^{10,14} shows with fair certainty is (XX); but this trimeric form is apparently only

* The usual methods of fractional distillation, dehydrogenation and degradation leave much to be desired in ascertaining all the isomeric components of the heterogeneous dimeric, trimeric, etc., fractions.

¹¹ Vaughan, *J. Amer. Chem. Soc.*, 1932, **54**, 3868.

¹² Harkness, Kistiakowsky and Mears, *J. Chem. Physics*, 1937, **5**, 682.

¹³ Alder and Rickert, *Ber.*, 1938, **71**, 373, 379.

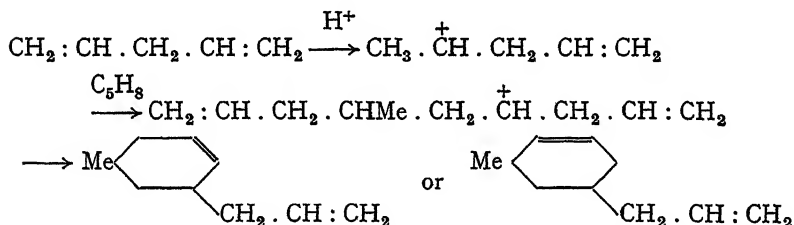
¹⁴ Farmer and Martin, unpublished work.

one of a number of isomeric forms, the nature of which are still undetermined. It is easy to represent the formation of the acid-formed dimeric and trimeric forms (XI) and (XX) in terms of Whitmore's hypothesis, but to do this the directions of ethylenic polarisation controlling the addition reactions have to be arbitrarily selected—a course which seems unsatisfactory, unless the dimeric and trimeric forms which have as yet escaped isolation correspond to other polarisations.

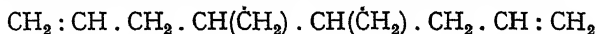
Acid-catalysed 2:3-dimethylbutadiene represents an interesting example in which the dimeric (29.0 per cent.), trimeric (19.5 per cent.), tetrameric (18.4 per cent.) and pentameric (15.0 per cent.) fractions can easily be isolated in a state of high purity (in approximately the yields indicated) by ordinary fractional distillation followed by continuous evaporative distillation.¹⁴ The very viscous residue then consists almost entirely of hexamer. There is as yet no information regarding the degree of structural heterogeneity reached in the tetrameric and higher polymers.

Thermal Polymerisation of Unconjugated Dienes.

The only simple unconjugated diene the polymerisation of which it has been at present possible to examine in detail is $\Delta^1:4$ -pentadiene, $\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2$, which on the basis of Whitmore's hypothesis might reasonably be expected to give 1-methyl-3-allyl-*cyclohexene* in an acid medium :



Actually it has not been polymerised successfully in acid solution, nor has it given low-molecular polymers with boron trifluoride. When heated, however, at 270° C. it has been found to give a series of polymers ranging up to the tetramer at least, and of these the dimer has proved to consist, not of 1-methyl-3-allyl-*cyclohexene*, but of the corresponding 1-methyl-2-allyl compound. The reason for the formation of the latter is not immediately obvious: it might conceivably mean that a 2-2'-bond between the pentadiene molecules is first established (either additively with hydrogen separation, or by thermal conversion of the monomers into free-radical forms which unite to give first the diradical



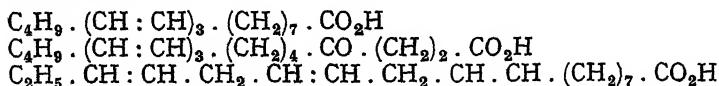
and ultimately the stabilised cyclic dimeride) or alternatively that a portion of the pentadiene is isomerised to piperylene before polymerisation sets in. Although no experimental evidence has been obtained that isomerisation here precedes dimerisation, it is to be noted that the very similar hydrocarbon diallyl, according to Lebedev and Slobodin,¹⁵ reaches equilibrium with its conjugated isomeride dipropenyl when heated to 205° in presence of floridin. Hence isomerisation may well play a part in the polymerisation of pentadiene (and therefore also in the

¹⁵ Lebedev and Slobodin, *J. Gem. Chem. Russ.*, 1934, 4, 123.

analogously unsaturated long-chain acids of the linoleic-linolenic series), but the mechanism of heat-isomerisation itself requires to be elucidated and may perhaps depend on the production of free-radical forms.

Thermal Polymerisation of Trienes.

Experiments with triolefinic hydrocarbons have been precluded by the inaccessibility of these substances in reasonably large quantities. Extended experiments have however been carried out with the esters of the long chain acids :¹⁸



in which the carboxyl groups are so remote from the unsaturated centres as probably to have no appreciable effect on the course of reaction. In these cases also thermal polymerisation gives a series of low-molecular polymers (chiefly dimers and trimers), and although exact formulation of the products is here more difficult, the results leave slight doubt but that the structures are cyclic ones and are closely comparable to those described above. Here, however, the monomer also undergoes cyclisation.

The results thus show that a considerable diversity of structure is possible amongst the cyclic polymers of diolefines, and at present a satisfactory elucidation and correlation of the multiple lines of polymeric reaction remains to be put forward.

Acknowledgments are made to Imperial Chemical Industries, Ltd. for permission to include certain of the examples quoted above.

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¹⁸ Farmer, Sunderland, Morrison-Jones, and Hilton, unpublished work.

DIMERISATION OF PETROLEUM HYDROCARBONS.*

BY W. J. SPARKS, R. ROSEN AND PER K. FROLICH.

Received 24th March, 1939.

The petroleum industry has in recent years become intensely interested in polymerisation as a technique for extending the possibilities in the processing of hydrocarbons. The polymerisation methods which now are being rapidly adopted in refinery operations have two extremely important elements of usefulness: (a) they make possible the conversion into more valuable materials of the increasing quantities of gaseous degradation products from cracking operations, and (b) they permit of

* Contribution by the Chemical Laboratories of the Standard Oil Development Company.

a considerable degree of control over the molecular structure of the materials produced, thereby enabling the petroleum technologist to meet specific requirements of product quality to an extent considered impossible only a few years ago.

Although polymerisation of petroleum unsaturates is now being employed for the synthesis of such varied products as fuels, lubricants, and plastics, the most important application to date from the standpoint of volume is in the manufacture of gasoline of high octane number. On account of certain volatility requirements which have to be met in this instance, dimerisation, rather than polymerisation in general, is of most importance at the present stage of the development. This is illustrated by the current large scale production of commercial *isooctane* via either the dimer of *isobutene* or the so-called "co-dimer" of *isobutene* with one or the other of the normal butenes. In view of the industrial importance of these processes, the authors consider it particularly opportune to use them as the background for a discussion of dimerisation of unsaturated hydrocarbons.

Dimerisation of Butenes.

1. Dimer of *Isobutene*.

The method employed commercially^{1, 2} for dimerising *isobutene* consists of absorbing this olefin selectively, out of a mixture* of butanes and butenes previously fractionated from refinery gases, in aqueous sulphuric acid of about 65 per cent. strength at room temperature ("cold-acid" process), and of heating the resulting acid-olefin extract to 100°-125° C. Presumably the extract contains a mixture, more or less in equilibrium, of olefin, mono-alkyl sulphate, di-alkyl sulphate, and alcohol (*i*-butyl alcohol). The exact route of the polymerisation reaction is not known. In any event, there separates, on heating, an oily layer containing some 70 per cent. of dimer, the remainder being largely trimer with some higher boiling material. The dimer is hydrogenated to produce *iso*-octane for use in gasoline.

Fractional distillation of a narrow fraction, representing some 80 per cent. of this hydrogenated product, showed it to consist of 90 per cent. of substantially pure 2, 4, 4-trimethylpentane and 10 per cent. of a mixture of 2, 4, 4-trimethylpentane (B.P. 99° C., n_D^{20} 1.3916) and 2, 3, 4-trimethylpentane (B.P. 111.5° C., n_D^{20} 1.4045).²

This analysis is in good agreement with the work of Butlerow,^{3, 4} who found that the dimer fraction of polymer, resulting from mixing liquid *isobutene* with 60 per cent. sulphuric acid and then heating for twenty-four hours at 100° C., consisted of 2, 4, 4-trimethylpentene-1 and 2, 4, 4-trimethylpentene-2. Whitmore and his associates^{5, 6, 7} subsequently separated these isomers by fractional distillation and confirmed their structure by ozonisation. McCubbin and Adkins⁸ showed that 2, 4, 4-trimethylpentene-1 is present in the dimer fraction in considerable excess over 2, 4, 4-trimethylpentene-2.

¹ S. H. McAllister, *Oil and Gas Journal*, Nov. 12, 1937, 36, 139.

² Bayway Refinery Operation—S.O.N.J.

* Henceforth referred to as refinery C₄ cut.

³ A. Butlerow, *Ann.*, 1877, 189, 44.

⁴ F. Wreden, *Ber.*, 1876, 9, 1605.

⁵ F. C. Whitmore and J. M. Church, *J.A.C.S.*, 1932, 54, 3710.

⁶ F. C. Whitmore and S. N. Wrenn, *ibid.*, 1931, 53, 3136.

⁷ C. O. Tongberg, J. D. Pickens, M. R. Fenske and F. C. Whitmore, *ibid.*, 1932, 54, 3706.

⁸ R. J. McCubbin and H. Adkins, *ibid.*, 1930, 52, 2547.

2. "Co-dimer" of Isobutene and Normal Butenes.

When the mixture of butenes present in refinery C_4 cut is caused to react with sulphuric acid of 63-72 per cent. strength at higher temperatures, 75°-100° C., absorption of the olefins and polymerisation take place in one operation. Under these conditions, the tendency is for the molecules of isobutene to combine with the molecules of either one of the normal butenes to give a "co-dimer" or cross-dimer.⁹ As this method of operation, the so-called "hot-acid" process, roughly doubles the yield of commercial isooctane that can be obtained from a given quantity of isobutene, with only a nominal decrease in octane number, it has become more important from an industrial standpoint than the previously described "cold-acid" process. The dimer* fraction constitutes about 85 per cent. of the total polymer.

In general, the hydrogenated product of the dimer resulting from cross-polymerisation of the unsaturates in refinery C_4 cut varies within wide limits, depending upon variations in its manufacture.⁹ There is, of course, the possibility that isomerisation may occur in the hydrogenation step, so that the conditions of hydrogenation also may play a rôle in the composition of the hydrogenated product. On the basis of a fractional distillation of one sample, the composition shown in Table I was deduced.

According to Whitmore, Laughlin, Matuszeski, Crooks, and Fleming,¹⁰ the product of the cross-polymerisation of isobutene with mixed *n*-butenes (from dehydration of butanol-2) contained chiefly 2, 2, 3-trimethylpentene-3, together with its rearrangement product, 2, 3, 4-trimethylpentene-1.

TABLE I.

Hydrocarbon.	Approx. Per Cent. of Plateau.	From this Analytical Distillation.		From Literature.	
		B.P. °F.	R.I.	B.P. °F.	R.I.
2, 4, 4-Trimethylpentane .	4	212-214	1·390-1·392	210·7	1·3916
2, 5-Dimethylhexane .	6	227-229	1·398-1·399	228·5	1·3929
3, 3-Dimethylhexane .	5	230	1·399-1·400	231·8	1·3998
2, 2, 3-Trimethylpentane .	7	230-231	1·400	231·5	1·4030
2, 3, 4-Trimethylpentane .	18	232-234	1·400-1·402	232·7	1·4045
2, 3, 3-Trimethylpentane .	22	234-237	1·402-1·404	236·4	1·4074
2-Methyl-3-Ethylpentane .	18	237-238	1·404-1·405	237·2	1·4016
2, 3-Dimethylhexane .	—	238	1·405-1·410	237·2	1·4095

3. Dimerisation of Normal Butenes.

There appears to be a scarcity of data on the separate polymerisation of the normal butenes. On contacting butanol-2 at 80° C. with 75 per cent. sulphuric acid for 48 hours, Drake and Veitch¹¹ observed that the dimer fraction of the resulting polymer consisted of 3, 4-dimethylhexene-2. The same dimer was obtained by Lebedev and Orlov¹² by polymerising butene-2 at room temperature over activated floridin for long periods of time.

⁹ Development and Research Laboratories, Standard Oil of Louisiana.

* According to the classical definition, we should hardly be justified in considering this a true dimer. However, the somewhat lax use of the term "polymerisation" has become so widespread in recent years that it would be futile to apply any kind of censorship on present day petroleum nomenclature in this field. It seems that a broadening in meaning of the terms is inevitable.

¹⁰ F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski, H. M. Crooks, Jr., and G. H. Fleming, A.C.S. Meeting, Organic Division Abstracts, p. 10, Pittsburgh, September 1936.

¹¹ N. L. Drake and F. P. Veitch, Jr., *J.A.C.S.*, 1935, **57**, 2623.

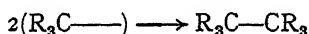
¹² S. V. Lebedev and S. M. Orlov, *J. Gen. Chem. U.S.S.R.*, 1935, **5**, 1589; *C.A.*, 1936, **30**, 2169.

Hoog, Smittenberg, and Visser¹³ state that the hydrogenated dimer fraction of the polymer, obtained by polymerisation of *n*-butenes (made by dehydration of butanol-2) over a phosphoric acid catalyst, supported on a carrier at 170° C. and 10 atmospheres pressure, consisted of a mixture of 2, 3, 4-trimethylpentane, 2, 2, 3-trimethylpentane, and 2, 5-dimethylhexane. They ascribe the occurrence of these three *iso*-octanes to the fact that, prior to polymerisation, the *n*-butenes isomerise to *isobutene*, which, in turn, cross-polymerises with the *n*-butenes. In any event, these products are in accord with those identified as constituents of the "co-dimer" fraction of polymer from *isobutene* and normal butenes (see Table I).

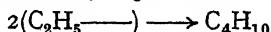
Mechanism of Dimerisation.

Before proceeding to the observations on the dimerisation of other unsaturates, it may be well to consider the possible mechanism involved in this type of reaction. Dimerisation of a simple olefin clearly involves the formation of new C—C bonds between separate molecules. It is evident therefore that, at the moment of closure, a combination of the two active molecules must involve an abnormal condition of the respective carbon atoms. To present an adequate discussion of the various mechanisms proposed to account for what takes place during dimerisation and of the tremendous amount of supporting data is out of the question in view of the limited space allotted to this paper.

The simplest type of dimerisation appears to be that of direct linkage of free radicals :



The existence of simple radicals was demonstrated by Paneth and Lautsch,¹⁴ and Rice and co-workers.¹⁵ The former showed that the ethyl radicals, formed by thermal decomposition of tetraethyl lead, yield butane when condensed by liquid air :



The existence of more complicated free radicals was first demonstrated by Gomberg, who found that hexaphenylethane¹⁶ exhibited peculiar properties; Schlenk and co-workers¹⁷ later showed free radical formation, in the particular case of hexabiphenylethane, to involve spontaneous cleavage of the molecule to give two identical fragments.

In the case of the highly substituted free radicals, combinations may involve not only simple union of active molecules to form reversible dimers but also rearrangements in which shifts of free bonds may occur. Thus, Marvel and his co-workers^{18, 19} have shown that tetraphenyl-ditertiary butylethynylethane may be completely converted into a diallene by heating. They assume rearrangements involving the formation of unexpected free radicals as follows : *

¹³ H. Hoog, J. Smittenberg and G. H. Visser, *2nd World Petroleum Congress Proc.*, 2, (2), 489, Paris, June, 1937.

¹⁴ F. Paneth and W. Lautsch, *Ber.*, 1931, 64, 2702.

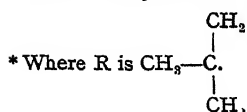
¹⁵ F. O. Rice, W. R. Johnston and B. L. Evering, *J.A.C.S.*, 1932, 54, 3529.

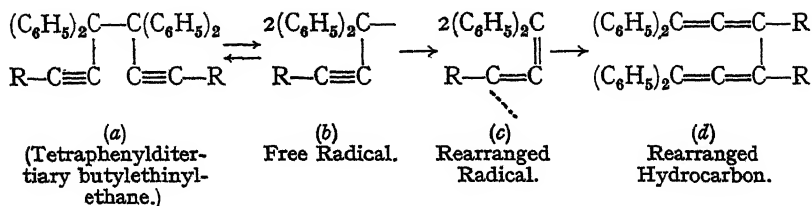
¹⁶ M. Gomberg, *Chem. Rev.*, 1924, 1, 91.

¹⁷ W. Schlenk, T. Weickel and A. Herzenstein, *Ann.*, 1910, 372, 1.

¹⁸ W. J. Sparks, W. J. Peppel and C. S. Marvel, *J.A.C.S.*, 1937, 59, 1351.

¹⁹ E. D. Farley and C. S. Marvel, *ibid.*, 1936, 58, 29.

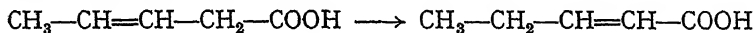




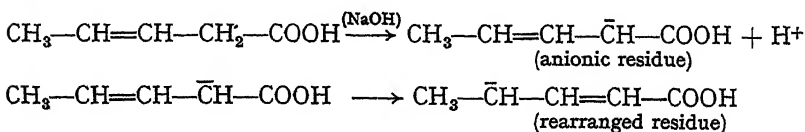
No molecules having unsymmetrical structures corresponding to the union of rearranged groups with unchanged free radicals (*i.e.* union of *b* and *c*) have been observed among the products of the above reactions. This shows that the rate of shifting of free valencies, once they are formed, may be very rapid. It therefore appears likely that, although every union of monomeric species to form dimers must necessarily involve the combination of free carbon valencies, a proper understanding of dimerisation phenomena must require consideration of rearrangements which may accompany the reaction and correspondingly determine the structure of the resulting product.

It is proposed here that the molecular rearrangement characterising dimerisation of olefins as contrasted to dimerisation of free radicals involves a shift, from one monomer, of a hydrogen atom which ultimately appears in the dimer molecule attached to the other combining monomer on the previously unsaturated carbon atom which is adjacent to the newly formed bond. In intramolecular changes, this is conveniently designated a 1, 3 rearrangement. The 1, 3 rearrangement to give isomers may involve either free valencies or, more frequently, protons or anions. The latter rearrangements are designated, respectively, prototropic and anionotropic.

The earliest example of prototropic rearrangement is in the work of Fittig,^{20, 21} who observed the conversion of β , γ -pentenoic acid to α , β -pentenoic acid, as follows:



Lapworth²² interpreted this shift of bonds in unsaturated acids by assuming a migration of the mobile hydrogen in the form of a proton, leaving an anionic residue in which the negative charge is redistributed, as shown below:



Mechanisms proposed by Burton, Ingold, Lowry and others^{23, 24, 25, 26, 27} have involved the assumptions that rearrangements of the above type may be intramolecular or intermolecular. It is of interest to note here

²⁰ R. Fittig, *Ber.*, 1891, **24**, 82.

²¹ *Ibid.*, 1894, **27**, 2677.

²² A. Lapworth and A. C. O. Hann, *J.C.S.*, 1902, **81**, 1508.

²³ T. M. Lowry, *ibid.*, 1899, **75**, 211.

²⁴ H. Burton, *ibid.*, 1930, **248**; 1928, 1650.

²⁵ G. A. R. Kon and C. J. May, *ibid.*, 1927, 1549.

²⁶ H. Burton and C. K. Ingold, *ibid.*, 1928, 904.

²⁷ J. W. Baker, *ibid.*, 1928, 1583.

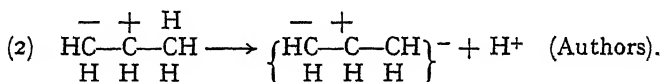
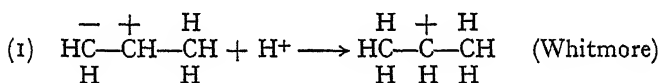
that the former, involving only one molecule, would be expected to give isomeric monomers, whereas a 1, 3 shift involving two molecules might be expected to lead to dimers through the union of an anionic residue to another molecule with the subsequent addition of a proton to the resulting dimer radical. That radicals do add to double bonds was demonstrated by Conant and Scherp²⁸ who showed that triphenylmethyl adds readily to isoprene and to dimethylbutadiene.

The simple prototropic rearrangement of Fittig does involve the formation of a new C—C bond but, since only adjacent carbon atoms are involved, this has become accepted as merely a necessary corollary to the well-known behaviour of the three-carbon system. Intramolecular formation of new bonds between non-adjacent carbon atoms has, however, been demonstrated by Baker²⁹ in the equilibrium between the trimethyl ester of 1, 1, 2-tricarboxypropene-1 and its cyclopropane isomer, and by Ingold, Perren, and Thorpe³⁰ in the case of the equilibrium between similar cyclobutane derivatives and their straight chain isomers. The latter suggest that the equilibria involved in such reactions may be reversible.

These ring-chain equilibria have generally been accepted as being related to the simpler forms of prototropism. Since they involve non-adjacent carbon atoms, it now appears that an extension of the principles of prototropism to cover intermolecular combinations is justified.

Stewart and Graham³¹ have proposed that a catalyst may influence prototropic changes in either of two ways, *i.e.* (1) it may facilitate the withdrawal of a proton from the parent molecule, or (2) it may promote the addition of a proton to the ion.

The explanation presented here, as an extension of the views of Lowry and others on prototropism, is applicable to any polymerisation process and essentially involves separation of a proton from an unsaturated molecule. It differs from the dimerisation concept of Whitmore³² in that he dealt only with acid polymerisation and assumed that the activation of the molecules involved addition of an external proton to the system. These concepts are illustrated below:



Either mechanism may be used to explain dimerisation phenomena in acid media. However, it will be recalled that the original prototropic rearrangement of Fittig^{20, 21} was carried out in alkaline solution, and Lowry regards bases as being chiefly proton removers.

Other explanations have involved the addition of catalysts to one of the C=C carbon atoms, with the formation of either electron excess or

²⁸ J. B. Conant and H. W. Scherp, *J.A.C.S.*, 1931, **53**, 1941.

²⁹ J. W. Baker, *J.C.S.*, 1935, 188.

³⁰ C. K. Ingold, E. A. Perren and J. C. Thorpe, *ibid.*, 1922, 1765.

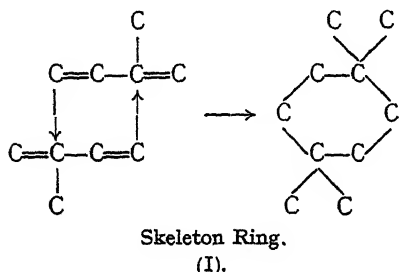
³¹ A. W. Stewart and H. Graham, *Recent Advances in Organic Chemistry*, 2, 395: Longmans, Green & Co., N.Y., 1936.

³² F. C. Whitmore, *Ind. Eng. Chem.*, 1934, **26**, 94.

electron deficient residues.³³ These may then add to monomers to form polymers.

It will be observed that all of these proposals involve the formation of an active intermediate under the influence of catalysts. Regardless, however, of the character of the active residue, the ultimate dimerisation products result from the shift of a hydrogen atom to a gamma position, and formation of new bonds between carbon atoms of the active nucleus and a monomer molecule.

Wachter³⁴ has proposed a series of rules for predicting the orientation of lower olefins in forming dimers. Thus, he points out that the least substituted double-bonded carbon atom contributes the hydrogen atom and that the resulting free bond adds to the most substituted double-bonded carbon atom. These rules are supported by many examples, but some modification appears necessary in the case of isoprene which according to these rules, should combine as in (I).



Three other six-membered ring structures have been observed,³⁵ but not this one. Likewise, these rules do not appear to explain the formation of tetramethylethylene from propylene,⁴⁴ and the addition of acetylene to vinylacetylene to form divinylacetylene.³⁸

From the standpoint of products, olefins may dimerise in at least three different ways to produce, respectively, (1) straight chain dimers, (2) cyclobutane rings, and (3) cyclohexane rings. It has been proposed by Egloff³⁶ that the type of dimer formed depends upon the number of double bonds, in the monomer molecules, and their position in respect to each other. However, a review of the literature shows that the simple classification proposed is not generally applicable since there are instances, discussed below, which show that monomers may dimerise in two classes (*e.g.* isoprene^{35, 37} or vinylacetylene).^{38, 39, 40}

There are numerous literature references on the polymerisation of unsaturated hydrocarbons. These have been well summarised in the books of Egloff,³⁶ Burk,⁴¹ and Whitmore,⁴² and some polymerisation reactions are discussed in detail in recent articles.^{34, 13, 33}

³³ P. J. Flory, *J.A.C.S.*, 1937, **59**, 241.

³⁴ A. Wachter, *Ind. Eng. Chem.*, 1938, **30**, 822.

³⁵ T. Wagner-Jauregg, *Ann.*, 1931, 488, 176.

³⁶ G. Egloff, *Reactions of Pure Hydrocarbons*, A.C.S. Monograph Series, (73); Reinhold Publishing Corp., N.Y., 1937.

³⁷ T. Midgely, Jr., and A. L. Henne, *J.A.C.S.*, 1929, **51**, 1294.

³⁸ J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, *ibid.*, 1931, **53**, 4197.

³⁹ M. E. Cupery and W. H. Carothers, *ibid.*, 1934, **56**, 1625.

⁴⁰ H. B. Dykstra, *ibid.*, 1934, **56**, 1625.

⁴¹ R. E. Burk, H. E. Thompson, A. J. Weith, I. Williams, *Polymerization*, A.C.S. Monograph Series, 75; Reinhold Publishing Corp., N.Y., 1937.

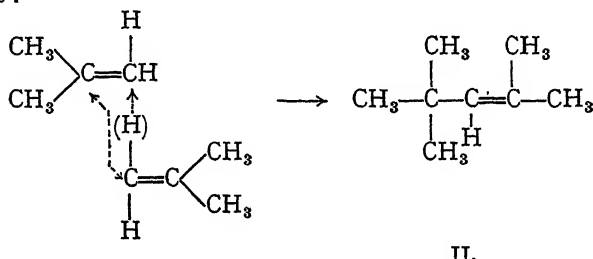
⁴² F. C. Whitmore, *Organic Chemistry*; Van Nostrand Co., N.Y., 1937.

Dimerisation Reactions.

This section discusses the application of the proposed mechanism, involving 1, 3 rearrangement of a hydrogen atom, to some of the known dimerisation reactions. Since intramolecular equilibria between isomers are a function of the thermodynamic conditions under which the isomers result, no attempt is made to account for isomers where only a change in the position of the double bond is involved.

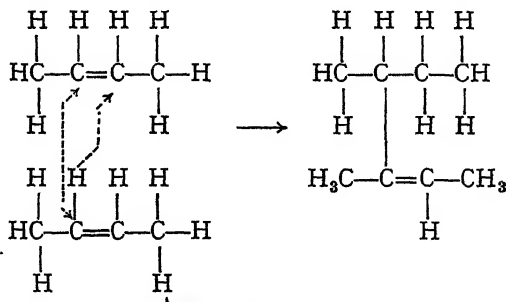
1. Olefin Dimers.

Isobutene.—It has been shown earlier in the paper that the polymerisation of *isobutene* gives a mixture of 2, 4, 4-trimethylpentene-1 and -2. This involves a shift of a hydrogen atom, which may be shown as follows :

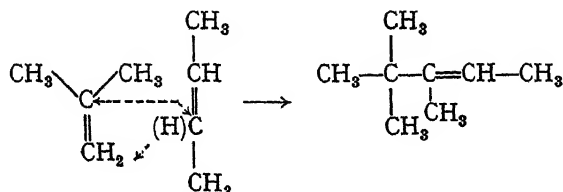


It seems appropriate to mention here that, although di-*isobutene* (II) may be polymerised, by contact with clay, to tetramer, neither of the polymers can be an intermediate in the formation of long chain molecules. This is borne out by experiments in these Laboratories which show that neither dimer nor tetramer gives high polymers under conditions favourable to such a reaction using isobutene alone, and that even small amounts of dimer or tetramer in the monomer effectively inhibit the reaction. It is apparent not only that, in forming high polymers, an active radical²² must exist intermediate between I and II, but also that conditions favourable to formation of II must be eliminated.

Butene-2.—The formation of 3, 4-dimethylhexene-2 as the main dimer fraction in the polymerisation of *n*-butenes from¹¹ butanol-2 is also in accord with the proposed viewpoint. The reaction is illustrated as follows :



Cross-Polymerisation of Isobutene and *n*-Butenes.—Products reported for cross-polymerisation of mixed butenes indicate considerable isomerisation. Of the two products reported by Whitmore,¹⁰ 2, 2, 3-trimethylpentene-3 would be expected and is obtained as a normal dimerisation product :



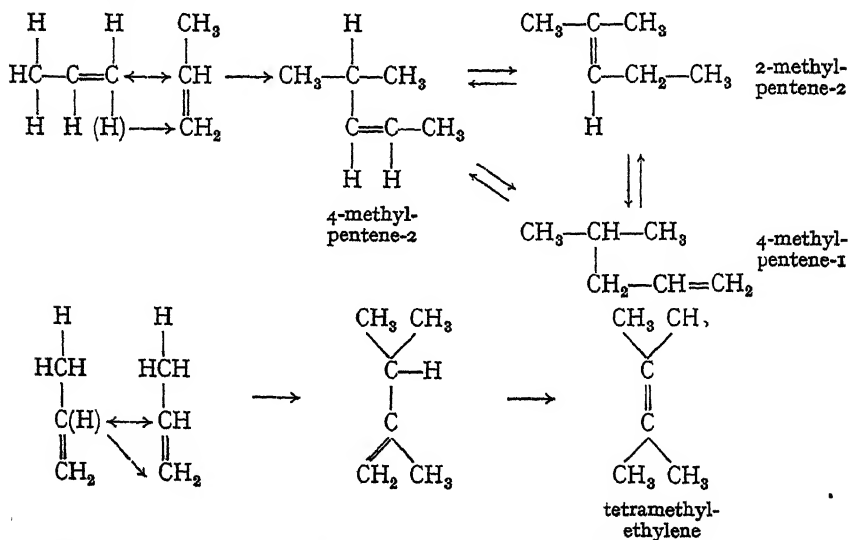
The product 2, 3, 4-trimethylpentene-1, obtained in small yields, would appear to be a secondary rearrangement product.

Propene.—There is little information on the formation of dimer in most of the papers on the polymerisation of propene. Wachter³⁴ observed that the hexene fraction of the polymer produced at 200° C. and 1000 pounds pressure over a supported phosphoric acid catalyst consists principally of 2-methylpentene-2 and 3-methylpentene-2.

Gilliland and Monroe⁴³ obtained a 30-40 per cent. yield of polymer boiling in the hexene range by polymerisation of propene with 25-30 per cent. phosphoric acid at 275-300° C. and 2000-3000 pounds pressure, and also found that the hexene fraction consisted largely of 2-methylpentene-2 and 3-methylpentene-2.

Polymerisation of propene over an alumina-on-silica catalyst at 160° C. and ten atmospheres pressure gave a polymer, 50 per cent. of which consisted of hexenes.¹³ Although the hexenes were not identified as such, it was shown that the main component of the hydrogenated product was 2-methylpentane. Whitmore and Marschner⁴⁴ found 2-methylpentene-2 and tetramethylethylene as the principal products of the hexene fraction in the polymerisation of propene at 350° C. in the presence of an alumina-on-silica catalyst. Brooks⁴⁵ reported the production of 4-methylpentene-1 by 90-92 per cent. sulphuric acid polymerisation of propene at 25° C. in the presence of spindle oil.

These data are in general accord with the 1, 3-rearrangement of a hydrogen atom as shown below:

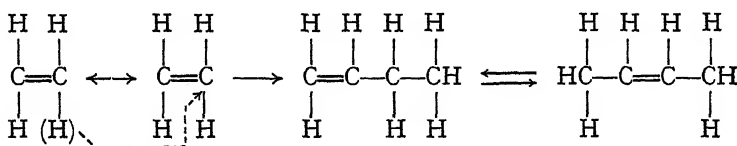


⁴³ E. R. Gilliland, and L. A. Monroe, Unpublished Work at M.I.T., 1936.

⁴⁴ F. C. Whitmore and R. F. Marschner, A.C.S. Meeting, Petroleum Division Abstracts, p. 6, N.Y., April, 1935.

The 3-methylpentene-2 reported by Wachter³⁴ and by Gilliland and Monroe⁴³ would appear to be a secondary rearrangement product.

Ethylene.—It has been shown⁴⁶ that butene-2 is obtained when ethylene is polymerised at 8-10° C. at fifty atmospheres pressure in the presence of BF_3 catalyst, whereas butene-1 is largely obtained by passing ethylene through a high frequency discharge at 10° C.⁴⁷ The shift of a hydrogen atom, during the polymerisation of ethylene, to produce butene-1 or -2 is illustrated as follows :

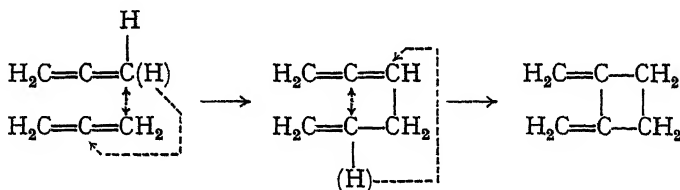


With increasing temperatures of polymerisation, particularly in the absence of catalysts, secondary reactions result; thus, the products obtained from ethylene vary considerably depending upon the conditions of polymerisation (Wheeler,⁴⁸ Schneider, and Frolich).⁴⁹

2. Diolefin Dimers.

Dimerisation of allene and its derivatives is characterised by the formation of one or more unsaturated derivatives of cyclobutane. Lebedev and Merezhkovskii report⁵⁰ that the polymer resulting on heating allene for $3\frac{1}{2}$ days at 140° C. under 100 atmospheres pressure contains 5 per cent. of a dimer consisting of 1, 2-dimethylene cyclobutane.

This allene dimer readily results according to the proposed shift of a proton between two molecules as illustrated below :



Lebedev and Skavronskaya⁵¹ polymerised butadiene in a sealed tube for ten days and obtained 1-ethenylcyclohexene-3. Lebedev and Sergienko⁵² reported the formation of a dimer fraction, consisting of mainly 1-ethenylcyclohexene-3 and a small amount of its isomerisation product, 1-ethenylcyclohexene-1, upon heating butadiene for 120 hours at 100° C.

⁴⁶ M. Otto and L. Bub, U.S. Patent 1,989,425, Jan. 29, 1935.

⁴⁷ G. Mignouac and R. V. de Saint-Aunay, *C.r.*, 1929, 189, 106.

⁴⁸ R. V. Wheeler and W. L. Wood, *J.C.S.*, 1930, 1819.

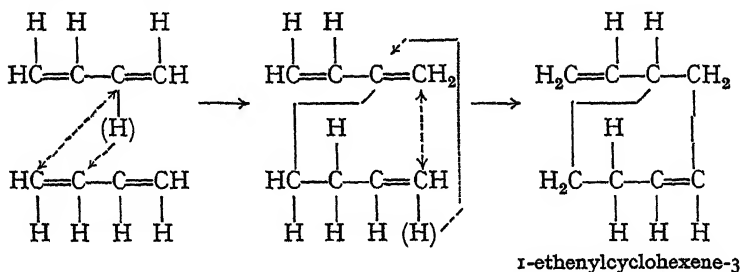
⁴⁹ V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, 1931, 23, 1405.

⁵⁰ S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1249; *C.A.*, 1914, 8, 320.

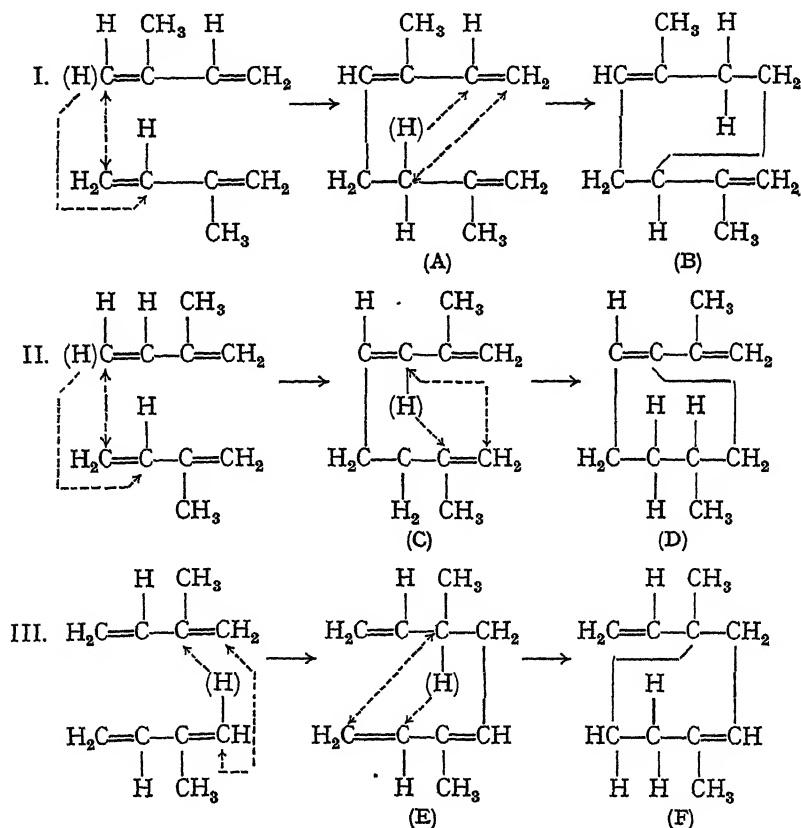
⁵¹ S. V. Lebedev and N. A. Skavronskaya, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1124; *C.A.*, 1912, 6, 855.

⁵² S. V. Lebedev and S. Sergienko, *Compt. rend. acad. sci. (U.S.S.R.)*, 1935, 3, 79.

Formation of these dimers in accordance with a 1, 3 rearrangement is illustrated below:



The polymerisation of isoprene by heat to give cyclic dimers³⁵ is explained as follows:

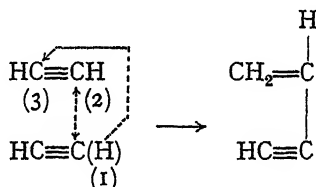


The structures A, C, and E were originally written for the purpose of illustrating the formation of the cyclic dimers of isoprene B, D, and F reported by Wagner-Jauregg.³⁵ These intermediates have not been observed. It is of interest to note, however, that the straight chain dihydro dimers (2, 6-dimethyloctadiene-2, 6; 2, 7-dimethyloctadiene-2, 6; and 3, 6-dimethyloctadiene-2, 6) reported by Midgely and Henne³⁷ have

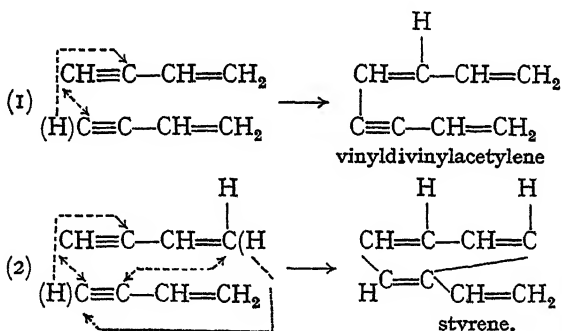
skeleton structures (exclusive of double bonds) identical respectively with those of A, C, and E. These products were obtained by a process of arrested dimerisation carried out in the presence of potassium in alcohol, and clearly indicate that rings are closed in stages, passing through open chain dimer or activated dimer (radical) intermediates.

3. Acetylene.

The principal dimer of acetylene reported in the literature³⁸ is vinylacetylene. This is accounted for by dimerisation involving a 1, 3 shift of a hydrogen atom as follows:



Vinylacetylene may in turn undergo dimerisation to either vinyldivinylacetylene³⁸ or to styrene.³⁹ These reactions may be shown as follows:



Concluding Remarks.

Throughout this paper, an attempt has been made to present a view of dimerisation consistent with the observed facts, without particular regard to the molecular and extra-molecular influences which co-operate to produce the final results. It has been shown that most of the known products resulting from dimerisation of aliphatic unsaturated hydrocarbons can be explained by the 1, 3 rearrangement of hydrogen proposed here. However, it is to be pointed out that all of the possible reaction products that could be written according to this mechanism have not been reported in the literature and may not necessarily be formed.

A great deal of additional work will be required before we may hope to have a complete understanding of the mechanism of dimerisation and polymerisation. Wachter³⁴ has already pointed out that the degree of activation necessary for producing union between molecules may also be sufficient to produce rearrangement or isomerisation of the reacting olefins and the resulting dimer. Further desirable work on the mechanism of dimerisation will involve a careful study of the effect of specific reaction conditions, particularly with respect to temperature and catalysts.

Current activities throughout the industry, on isomerisation of paraffins and olefins, and on alkylation of paraffins with olefins, should yield much valuable information on the nature of changes involving carbon-carbon and carbon-hydrogen bonds, and thereby help to clarify our concept of unsaturated hydrocarbon dimerisation. In the meantime, our interpretation of the reaction mechanism is bound to be of a speculative nature.

The authors wish to acknowledge the assistance of W. R. Sprowls of these Laboratories in the preparation of this paper.

GENERAL DISCUSSION.*

Dr. A. Wasserman (London) said: I do not know whether Bergmann's paper relates to photochemical and catalysed polymerisations only, or whether thermal associations are also taken into account. At any rate it is worthy of remark in connection with bimolecular thermal diene syntheses (*e.g.*, the dimerisation of cyclopentadiene, or the reaction between cyclopentadiene and benzoquinone, α -naphthaquinone or acrolein) that the products¹ are not cyclobutane derivatives nor is there any experimental or theoretical indication that two consecutive reactions take place. Both the steric selectivity and the relatively small activation energies make it probable that the configurations of the transition state and of the final state are similar, *i.e.*, during a successful collision the reactants do not take up an "end on" but a "broad-side on" orientation.²

Bergmann is of the opinion that Hurd and Williams (*ref. 61* in Bergmann's paper) proved that dimeric keten is acetyl keten. It is, however, probable that dimeric keten is an equilibrium mixture.³ Hurd and Williams obtained only 1.4 g. pyruvic osazone from 7 cm.³ dimeric keten, and it is possible, therefore, that the equilibrium mixture contains only 8 per cent. or even less of acetyl keten.

Dr. G. Salomon (Delft) said: The mechanism of polymerisation reactions is not fully understood, but it is quite clear that the rate-determining factors are very complex. It is difficult to judge the reactivity of catalysts because, in some cases, the rate of the uncatalysed reaction is likely to be zero. There is, however, much evidence that catalysis is only caused in the presence of some impurities. Compounds in almost unlimited number are described as polymerisation catalysts, many of them being perhaps only carriers for the same type of active "impurity." It is surprising to learn from Wassermann's paper that sulphides have not already been claimed as catalysts. Actually 5 out of the 9 metal sulphides tabulated as new catalysts are mentioned in Burk's "Polymerisation," page 110, Index No. 813.

While only metal halides, which probably produce a different reaction mechanism, bring about an acceleration of many powers of ten, the catalytic effect of many other compounds is small; on the other hand, a continuous range of inhibitors is known, including slightly active compounds (*e.g.*, alcohols), as well as powerful inhibitors (*e.g.*, quinones, sulphur and sulphur compounds). It seems not unlikely that the *relative* catalytic effects summarised in Table II are produced by the compensation of an inhibitor effect.

* On the four preceding papers.

¹ See formulæ in *Trans. Faraday Soc.*, 1938, 34, 130.

² Cf. Guggenheim, *Trans. Faraday Soc.*, 1938, 34, 144; Benford and Wassermann, *J. Chem. Soc.*, 1939, 364. See also Alder, *Handbuch der Biologischen Arbeitsmethoden Abt. I, Chemische Methoden, Teil 2, 2. Hälfte, Heft 9*, p. 3190, and *Angew. Chem.*, 1937, 50, 510.

³ This conclusion is based on a comparison of the Raman spectrum of dimeric keten and of tetramethylcyclobutanedione.

There is some evidence that the low molecular weight polymers are not essential links in the polymerisation of dienes. On the other hand they are always formed as by-products in polymerisation reactions. Little is known as to their ability to co-polymerise and polymerise on standing. Farmer's paper opens interesting new possibilities. With a complete series of di- to hexamers isolated and highly purified it should be possible to attack this problem from both the kinetic and the purely organic experimental side.

Dr. B. Whipp (*Billingham*) said: Williams has described a useful method for predicting the structures of the polymerisation products of two olefines.

In the paper of Sparks, Rosen and Frolich it appears (see Table I) that a saturated dimer resulting from the cross-polymerisation of *iso*- and normal butylenes contained 18 per cent. of 2Me₃Et pentane. I think Williams' method would predict 2.2.3-triMe pentane as the main primary product. Now, whatever the secondary rearrangement products of 2.2.3-triMe pentane may be, one would hardly expect to find 2Me₃Et pentane among them, and if it really occurs a remarkable mechanism must operate which might be of some interest to the theoreticians. On the other hand, many of the isomers mentioned by Sparks, Rosen and Frolich have very similar boiling-points and refractive indices and if these alone have been used as a means of identification the results may not be altogether reliable.

Dr. E. H. Ingold (*London*) and **Dr. A. Wassermann** (*London*) (*communicated*): Salomon's contribution is based on misconceptions both of our paper and of the literature of the catalysis of polymerisations. To mention one example only on the 19 (not 9) metal sulphides listed by us, not any, so far as we know, have previously been shown to be catalysts for the conversion of low boiling olefines into hydrocarbons boiling in the range of commercial fuel. We are conversant with Burk's "Polymerisation" which is mentioned in footnote 1 of our paper. Index No. 813 on page 110 mentions not 5 sulphides but sulphides of "groups 2 and 7" and relates to the British Patent 345738 which is not cited by us, since it refers to the use of sulphides as catalysts for reactions involving hydrogen, not as catalysts for polymerisations.

Dr. E. Bergmann (*Rehoboth*), in reply (*communicated*): The data collected in my paper refer to photochemical and catalysed polymerisations only. It has, however, been pointed out that the—apparently thermal—heterodimerisation between ketens and olefines gives cyclobutane derivatives as the photo-dimerisation of certain olefines and of α , β -unsaturated carbonyl and carboxyl compounds. In view of this it may well be that the dimerisation of ketens too leads to cyclobutane derivatives, but no decisive proof for these structures has been advanced so far.

I quite agree with Wasserman's remark that the kinetics of cyclopentadiene dimerisation leave no room for the assumption that it occurs in two consecutive steps (at least of comparable speed). But the case of phenylbutadiene, which gives a rather unexpected dimerisation product, is obviously different from that of cyclopentadiene; a kinetic investigation of the behaviour of phenylbutadiene would perhaps be interesting.

Drs. Sparks, Rosen and Frolich (*communicated*): We are in agreement with the comments of Whipp concerning the unreliability of the identification of the isomers resulting from the cross-polymerisation of *iso*- and normal butenes based on the boiling-points and refractive indices.

We have pointed out that even fractional distillations of the hydrogenated product of such dimers show appreciable variations depending upon the variations in the manufacture of the dimer. Under the relatively high temperatures used in hydrogenations, marked rearrangements of the co-polymer may conceivably result.

A considerable amount of work remains to be done on the identification by exact methods of the isomers that are present in cross-polymerisation

of iso- and normal butenes. We have merely shown what isomers are indicated upon the basis of boiling-point and refractive indices of cuts obtained in the fractionation of one sample of such a hydrogenated dimer.

We further agree that the presence of 2-methyl-3-ethyl pentane could not be explained on the basis of the mechanism suggested by us. If subsequent work establishes its presence, the tentative explanation would be rearrangements resulting from the conditions of hydrogenation.

SECTION B. LUBRICANTS (MEDIUM MOLECULAR WEIGHT).

THEORETICAL AND EXPERIMENTAL RESEARCHES ON THE SYNTHESIS OF LUBRICANTS.

By M. G. HUGEL.

Received in French on 27th February, 1939, and translated by
DR. C. DERVICHIAN.

If we consider in abstract the necessity of a country to supply its requirements for a liquid fuel from its own resources, we can only justify the synthesis of lubricants if by science we can surpass the qualities of natural products, and if the knowledge which may be so gained gives a new impulse to the extraction of lubricant oils from petroleum. The possibility of doing better than nature, however, implies researches on the relation between the constitution of liquids and the properties of lubricants. The quality of a lubricant oil involves many very different properties, the viscosity-temperature relation, volatility, melting-point, greasiness, and thermal stability, resistance to alteration, etc. The major part of lubricant oils consisting of hydrocarbons, progress in the matter of lubrication is bound up with an exact knowledge of certain physical and chemical properties of hydrocarbons. The results have been obtained very slowly, in spite of very intensive work, carried out as much in industrial as in scientific laboratories. The reason is that it involved a region which has long escaped investigation: *i.e.*, a study of the liquid state. May an organic chemist contribute to our knowledge of liquids? We have tried to do so by modifying the properties of liquids by organic synthesis. These researches, as well as their possible application to the synthesis of lubricants, form the subject of the present communication.

Part I. Theoretical.

A Study of Some Physical and Chemical Properties of Hydrocarbons.

The first and most important researches refer more especially to the viscosity of hydrocarbons. Two important questions have to be solved:

1. How to obtain hydrocarbons with sufficient viscosity to be used as lubricants.
2. What structure should these hydrocarbons have to give a good viscosity-temperature curve.

In fact, it is apparent, from the literature on lubricant synthesis,

that the aim of the researches may be classified chronologically according to the above two questions.

I think that these two questions have been answered mainly qualitatively. The time has come to give quantitative precision. The law governing the relation of viscosity at a given temperature with the molecular weight (for example 20° C.) has been established by Dunstan and Thole :

$$\log \eta = \alpha + \beta M \quad . \quad . \quad . \quad . \quad (1)$$

The logarithm of the viscosity is a linear function of the molecular weight. One might attach to each atom or group of atoms a "logarithmic increment" of viscosity, and so calculate the viscosity of a molecule, knowing its structure. This equation shows that the logarithm of the viscosity of a molecule increases always to the same extent in a homologous series by introduction of CH_2 groups. The Dunstan and Thole equation is applicable only to substances of weak viscosity; it does not serve for substances of higher molecular weight. In some homologous series containing so-called "associated substances" (*e.g.*, diols) it does not apply even to the lower members. In my opinion Dunstan and Thole's equation is only a particular case of a general law.

Starting from the fact that the Dunstan and Thole equation applies when the substance follows the Andrade equation

$$\eta = Ae^{\frac{c}{T}} \quad . \quad . \quad . \quad . \quad (2)$$

in regard to variation of the viscosity coefficient η with temperature. I have stated the more general case of a substance for which the viscosity-temperature relation obeys the equation, given also by Andrade :

$$\eta = Ae^{\frac{c}{T-b}} \quad . \quad . \quad . \quad . \quad (3)$$

It follows that the Dunstan and Thole equation must be modified in the following way :

$$\log \eta - \frac{cb}{(T-b)T} = \alpha + \beta M \quad . \quad . \quad . \quad (4)$$

This expression (4) differs from Dunstan and Thole's law by the introduction of a correcting term

$$\frac{cb}{(T-b)T}$$

For $b = 0$ this term cancels and we find the particular case of substances with weak viscosity, *i.e.*, not associated or only weakly associated. The generalised Dunstan and Thole equation shows particularly that the logarithmic increment for the CH_2 group is nearly the same for all substances whatever their viscosity and the series to which they belong. Thus, we find for the lower terms of alcohols the normal value of 0.107, due to the introduction of one CH_2 group. The "higher terms," beginning from C_6 , follow neither equation (2) nor (1). By the introduction of the correcting term $\frac{cb}{(T-b)T}$ we find again the normal value 0.107.

$$n \text{ amyl alcohol : } \log \eta_{20} - 0.96396 = -0.3367$$

$$n \text{ octyl alcohol : } \log \eta_{20} - 1.0477 = -0.0141$$

$$\log \text{arithmic increment for } \text{CH}_2 \text{ group} \quad \frac{0.3226}{} = 0.1075$$

It is difficult to give a theoretical interpretation to the correcting term $\frac{cb}{(T-b)T}$. It is generally admitted that the aliphatic hydrocarbons are not associated, but nevertheless this term must be introduced for the latter also, as soon as the molecular weight exceeds a given value. I should like to emphasise another fact. It is well known that the introduction of chemically active functions in the hydrocarbon molecule gives rise to an increase in the viscosity. In some cases, however, this rule does not hold. Let us compare olive oil with aliphatic hydrocarbons of the same molecular weight. There is no doubt that the viscosity of olive oil is weaker. The theoretical consequences of this fact are great; in fact the aliphatic hydrocarbons are not supposed to be associated and the difference in viscosity does not lie in a difference in the state of association between the two types of substances. The explanation must be sought elsewhere, *e.g.*, in the presence of a dipole moment in the olive oil molecule, which seems to play its part in the phenomenon of viscosity in a different sense than that in which we have so far been accustomed to consider.

All these remarks are fully justified hereafter. We will now discuss the viscosity-temperature relation. Contrary to what was generally assumed at the beginning of these researches, that viscous substances should be sought, we think that the real solution consists in increasing the molecular weight as much as possible and increasing the viscosity only slightly; the weaker the viscosity, the weaker are the variations of the viscosity with temperatures. This is quite a general rule; the variations are bound to the absolute value of the coefficient.

For the precise comparison of the viscosity-temperature variation curves it is important to use a mechanism which is not based on any hypothetical assumption. Only so will synthesis make serious progress. To solve this problem we have used Andrade's law (3). Using the logarithm of the viscosity, this expression becomes

$$\log \eta = a + \frac{c}{T-b} \quad . \quad . \quad . \quad (5)$$

where

$$\log A = a.$$

By a change in the co-ordinates one can transform the expression (5) into

$$u \cdot v = c \quad . \quad . \quad . \quad (6)$$

where

$$u = \log \eta - a$$

and

$$v = T - b.$$

Equation (6) is that of a rectangular hyperbola whose asymptotes are the u and v co-ordinates, and in which c characterises the kind of curvature of the hyperbola. But all these hyperbola have a particular point for which $u = v$. This point is on the bisector of the co-ordinates; we shall indicate it by C . If now we substitute the hyperbola $uv = c$ in the old system of co-ordinates ($\log \eta$ and T), the point C will be found in C' and the distance of the point C' from the origin O will have the value

$$\overline{OC'} = \sqrt{(\sqrt{c} + b)^2 + (\sqrt{c} + a)^2}$$

$\overline{OC'}$ is not only a function of c (the shape of the curve) but also of a and b (the position of the curve). It is $\overline{OC'}$ which seems to us capable of giving the shape and the position of the curve, enabling us to compare viscosity curves with great precision.

By the application of this system of absolute viscosity index to homologous series, one finds that the point C' is situated on a straight line, so that the distance $\overline{OC'}$ increases with the molecular weight up to a certain value, which varies with the series. From that point a sudden jump occurs towards much larger values, when a new straight line appears. The sudden jump in the index value corresponds to a change in the form of the viscosity curves. In the C_4 and C_5 alcohols, for example, it corresponds to the transition from the Andrade formula (2) to the second formula (3).

It seems likely that a second sudden jump occurs for much higher molecular weights, the precise data for which are not yet available. One can see that the whole of the liquids obey some very simple law. It does not seem that there are fundamental differences, but only gradual differences from one series to the other, and in the same series from one term to the other with the increase of molecular weight.

Part II. Experimental.

As we have seen, the viscosity laws impose some unavoidable conditions which must be taken into account in a synthesis of lubricant oils. It follows particularly from an examination of the viscosity-temperature curves, that with increase of viscosity the term b is introduced in the Andrade simple law, and that, instead of the absolute temperature T , we find a fictitious temperature $T - b$. This is necessary, because by reason of the variation of c and A with the increase of the viscosity (variations which are not independent one from the other) large increments of viscosity become impossible. There is mathematically only one way, *viz.*, that which is used in Andrade's general formula (3) by which the value of T can be diminished.

The introduction of b leads to the displacement of the viscosity curve towards the origin in the $uv = c$ system, *i.e.*, towards the hyperbola part, where the variations of u (*i.e.*, of $\log \eta$ or the viscosity) become much stronger, and the viscosity curve becomes worse. We must then see in what series of hydrocarbons the values of b are the smallest. This is the case for the aliphatic hydrocarbons. To attain sufficient viscosity, one must rise very high in the molecular weights. At equal viscosities, *e.g.*, at 20° , the difference between the molecular weights of hydrocarbons belonging to series which contain more and more closed rings, becomes higher as the number of rings is the greater. It follows for other properties of these synthetic lubricants.

Paraffin oils having a higher molecular weight are distinguished by a higher flash point and by a lower vapour pressure. On the other hand, oils containing many rings and with lower molecular weights are thermally more stable, firstly, because of their low molecular weight and, secondly, owing to the fact that the presence of rings itself increases the thermal stability. The Conradson test depends on the hydrogen content of the oils; it is smaller for the aliphatic hydrocarbons.

The resistance to alteration increases with the hydrogen content. The physical and chemical properties affecting the quality of an oil do not vary in the same way with the constitution. Aliphatic hydrocarbons always combine the maximum of the former qualities, and a maximum of the latter. The maximum of those qualities which they lack are, moreover, not found in the intermediate structure oils, *i.e.*, natural oils, but are found in the polycyclic aromatic structure oils. These are thermally very stable, but show a great capacity for alteration, a bad viscosity curve, and a higher vapour pressure.

In practice we conclude that the constitution of an oil must be appropriate to the use for which it is destined. If an oil is destined for use

at temperatures below 300°, it must have an excellent viscosity curve, a high flash point and a weak carbon test, and it must be a purely aliphatic oil.

If an oil is needed which must volatilise in the course of use without leaving residues, oils of mixed character, uniting in variable proportions, rings, and aliphatic chains are more indicated. Lastly, in the case of very high-temperature lubrication, only polycyclic aromatic oils would be convenient. We have concentrated on synthesising on the one hand purely aliphatic oils containing no rings and, on the other hand, polycyclic aromatic oils. Natural oils occupy an intermediate place between these two extreme categories, neither of which is found in nature. It is the synthesis of paraffinic hydrocarbons of high molecular weight which has chiefly claimed our attention. Some of the present known methods have been avoided because they do not give definite structures. In fact, there exists only one method which may give molecules of homogenous

TABLE I.—SYNTHETIC PARAFFINIC OILS.

t° .	η poises.	$T-b$.	$\log \eta - a$.	c .
Sample 1.				
20	0.5599	119.5	$-0.25189 + 3.14 \rightarrow 2.98811$	357.1
29.90	0.33078	129.4	$-0.48048 \quad 2.75952$	357.1
40	0.21314	139.5	$-0.67134 \quad 2.46866$	344.4
50	0.14512	149.5	$-0.83820 \quad 2.30180$	344.1
75	0.06786	174.5	$-1.16840 \quad 1.97160$	344.1
95.40	0.042144	194.9	$-1.37527 \quad 1.76473$	343.1
Sample 2.				
20	5.028	119	$0.70140 + 3.02 \rightarrow 3.72140$	442.9
29.90	2.5979	128.9	$0.41462 \quad 3.43462$	442.7
40	1.4573	139	$0.16354 \quad 3.18354$	442.5
50	0.89544	149	$-0.04796 \quad 2.97204$	442.8
75	0.33647	174	$-0.47304 \quad 2.54696$	443.2
95.40	0.18125	194.4	$-0.74172 \quad 2.27828$	442.9
Sample 3.				
20.10	145.21	127.1	$2.16200 + 2.87 \rightarrow 5.03200$	639.6
29.90	63.389	138.9	$1.80201 \quad 4.67201$	639.6
40	29.655	147	$1.47209 \quad 4.34209$	638.1
50	16.106	157	$1.20699 \quad 4.07699$	640.1
75	5.506	182	$0.74084 \quad 3.61084$	657.2
95.50	1.9579	202.4	$0.29179 \quad 3.16179$	640.1

configuration; *viz.*, the polymerisation of active olefines. It is, however, somewhat doubtful if one can completely avoid ring formation.¹

There is, however, some natural material of high molecular weight resulting from the polymerisation of highly saturated hydrocarbons. Nature realises this synthesis in a much more homogenous way than man can do it; *e.g.*, rubber. We have very large thread-form molecules; the transformation into paraffinic hydrocarbons having lubricating properties needs two operations, first reduction of the molecular weight to a convenient value, secondly, saturation of the double bonds.

Hydrogenation of rubber has already been the object of numerous researches and patents; in fact, all these different procedures are justifiable by the fact that one can obtain everything, starting from rubber. If it is carried out under high hydrogen pressure in the presence of a catalyst at a temperature slightly above 200° three reactions take place

¹ See, *e.g.*, Waterman, *Trans. Faraday Soc.*, 1935, 251.

simultaneously: (1) reduction of the molecular weight or cracking, (2) cyclisation, and (3) hydrogenation. Keeping all things constant, it is the nature of the catalyst which determines the relation of the three reactions. The catalyst has generally a definite action on the cracking and on the hydrogenation. The cyclisation reaction is then the resultant of the two others. A catalyst having pronounced destructive properties and very small hydrogenating activity will give products of low molecular weight, strongly cyclised. Another catalyst which is mostly hydrogenating will give, on the other hand, substances of high molecular weight, feebly cyclised, and much hydrogenated. Both catalysts cannot be used for the object we want to attain. We need a catalyst which reduces the molecular weight very considerably, for example, from 10,000 to at least 2000 and which exercises its hydrogenating action only at those places where it is indispensable to avoid cyclisation. The ends of the

TABLE II.—HYDROAROMATIC OILS

t° .	η poises.	$T - b.$	$\log \eta - a$		$c.$
Fraction 170/180.					
20.15	0.19947	110.15	- 0.70012 + 3.08	2.37988	262.1
29.70	0.12716	119.70	- 0.89565 + 3.08	2.18435	261.5
40	0.085157	130.00	- 1.06978 + 3.08	2.01022	261.3
50	0.06108	140.00	- 1.21424 + 3.08	1.86576	260.9
75	0.032197	165.00	- 1.49218 + 3.08	1.58782	262.0
95.30	0.021415	185.30	- 1.66929 + 3.08	1.41071	261.4
Fraction 190/200.					
20	0.55869	100.6	- 0.25283 + 3.131	2.87817	289.5
20.70	0.2941	110.3	- 0.53149	2.59951	286.7
40	0.17488	120.6	- 0.75726	2.37774	286.8
50	0.11379	130.6	- 0.94391	2.18709	285.6
75	0.050761	155.6	- 1.29447	1.83653	285.8
95.40	0.031648	176.0	- 1.49966	1.63134	287.1
Fraction 260/270.					
20	5649.6	46.7	+ 3.75202 + 3.29	7.04202	328.9
29.70	367.87	56.4	+ 2.56569	5.85569	330.3
40	49.701	66.7	+ 1.69637	4.98637	332.6
50	10.47	76.7	+ 1.01996	4.30996	328.0
75	0.8663	101.7	- 0.06235	3.22765	328.3
95.40	0.2633	122.1	- 5.7963	2.71037	330.9

chains are particularly susceptible to engender cyclisation. In fact, if scission of the rubber molecule occurs, at the place of the division there is formation of highly unsaturated places, probably with the appearance of conjugated double bonds. At such places the catalyst must work to saturate and avoid cyclisation. Amongst all the catalysts examined, metallic sodium gives the best results. It degrades the rubber strongly and it can fix itself on the double conjugated bonds, saturating them under hydrogen pressure.²

After this first phase, which takes place about 270-280°, one can now put this product in the presence of a strongly hydrogenating and weakly degrading catalyst to ensure complete saturation, and to reduce the molecular weight to the desired value. For a given catalyst the temperature governs the molecular weight with such precision that one can calibrate the apparatus (of continuous hydrogenation) according to the viscosity

² See Hugel and Gidaly, *Bul. Soc. chim.*, 1932, 639.

of the oil which is desired. Nevertheless, it is advisable, before bringing it to the desired temperature, to maintain the oil at a lower temperature for a certain time so that a certain saturation may occur; this is easily accomplished if one uses the upper parts of the continuous hydrogenation autoclave as a heat-exchanger. Closely analogous results are obtained with vulcanised rubber. In this case, metallic sodium acts at the same time as a desulphuring agent; loss of sulphur is rapid and complete at 280° . The paraffinic oils (of which we give some properties in Table I for comparison with those of other oils, Table II) were prepared in this way.

GENERAL DISCUSSION.

Dr. F. C. Frank (*Cambridge*) said: In reply to Hugel's opening query I personally welcome anybody's contribution to the theory of liquids, and am particularly glad to see it applied to the practical problem of lubrication. But I feel he has rather flattered our mathematical intuition, and should like to draw a diagram to show a little more fully what he has done.

The ideal law $\eta = Ae^{c/T}$ is obeyed reasonably well by all liquids having simple molecules except some of those described as associated.*

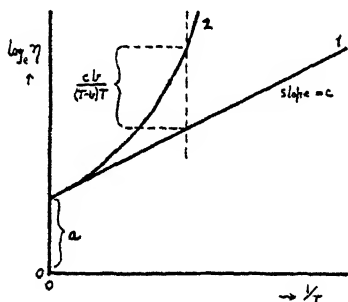


FIG. 1.

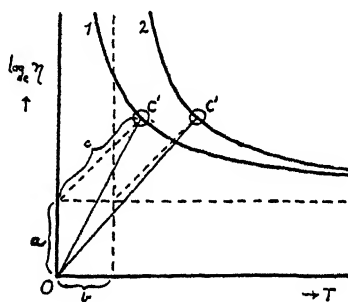


FIG. 2.

This gives the straight line in Fig. 1. Some cases, notably some of the "associated" liquids, and also the long chain derivatives, deviate from the ideal law, usually upwards as shown (Fig. 1, curve 2). Andrade found that a simple interpolation formula for some of the curves is $\eta = Ae^{c/(T-b)}$. The ordinary explanation given for the curvature is that a change in the type of liquid structure takes place over the temperature range, and b consequently measures both the temperature dependence of this change and the magnitude of its influence on viscosity.

By applying the correction $cb/(T-b)T$, Hugel reduces the actual viscosity to the value extrapolated by the ideal law from its course at high temperatures, and finds that these values conform to the additive relationships established by Dunstan and Thole for simpler molecules. *Thus at higher temperatures the long chain substances approach ideal behaviour both in respect of viscosity and its temperature dependence.*

In seeking the cause of the curvature in oils, I should remark that their molecules are far from spherical in form, so that increasing rotation must seriously change the packing. The higher hydroaromatics will be somewhat plate-like, while the long chain molecules are crumpled to a rather uncertain extent, which doubtless also depends on temperature. It would

* It should not be called Andrade's equation, having been given by Guzman in 1913 and discussed by various authors before Andrade.¹

¹ See Ward, *Trans. Faraday Soc.*, 1937, 33, 88.

be interesting to know whether very highly branched naphthenes, being more nearly spherical, have lower values of b .

Plotting $\log \eta$ directly against T , we obtain the hyperbolæ of Fig. 2. The position of point C' , below which the viscosity appears to rise much more rapidly, is clearly important for the comparison of various oils: but it is of less fundamental significance than one might at first suppose, for the viscosity to which it corresponds for a given oil depends on the base of logarithms and the temperature scale used. In any case I cannot follow Hùgel in attaching much importance to the distance OC' , and would consider it best to specify a , b , and c in every case.

Dr. G. Salomon (Delft) said: For those interested in the chemistry of rubber Hùgel's paper opens several new aspects. It would be valuable to learn what is the extent to which the pre-treatment of rubber (*e.g.*, mastication and acetone extraction) influences the hydrogenation reaction and the physical state of the reaction product. Furthermore, it would be interesting to learn more about the classification of catalysts, apart from the action of metallic sodium.

Prof. G. Hùgel (Strasbourg), in reply, said: Frank's attempt to give a physical interpretation to the viscosity-temperature relationships by reference to the ideas of normal and associated liquids is not well founded.

(1) Up to the present, physicists have only been able to examine the lower members of the organic series and these are, from the point of view of organic chemistry, exceptional. The great majority of organic substances remain uninvestigated. Before seeking to establish a theory of the liquid state it is especially important to study a greater number of liquids and particularly those having a higher molecular weight than those so far examined. It would be necessary then to classify them in order to ascertain the diversity of phenomena which they present.

(2) It is important to realise that, on our present information, when considering only their viscosity-temperature curves, many so-called "associated" liquids can quite well be taken for "normal." Furthermore, as we go up a series towards higher molecular weights, "non-associated" can behave as "associated" liquids. We must therefore first give a precise meaning to the terms "non-associated" and "associated."

With regard to Frank's remarks on my definition of an absolute viscosity index, I would say that the conception is of industrial importance, aiming at the definition of a viscosity curve by a single figure so that the curves of products having very different viscosities can be compared. So far, the methods of Dean and Davies and the viscosity rod of Ubbelohde have been used. These methods are based on unproved hypotheses; in particular they assume that different oil fractions of the same cut have the same viscosity index; in consequence of which false conclusions are drawn from them. The synthesis of lubricants can only make serious progress if research is based on a system of comparison of viscosity curves which makes no call on hypothesis and depends solely on mathematical considerations. We propose such a system; we do not pretend it is the only one; undoubtedly there are others; but it is based on comparison and, even if somewhat conventional, that fact does not affect the principle nor prejudice the deductions which can be drawn.

With regard to Salomon's question, oils prepared from different rubbers exhibit relatively few differences owing to the great reduction of molecular weight brought about during the preparation of the oils.

In reply to the President's question, the viscosities were determined in the Beaume-Vigneron apparatus. It is important to avoid making the determinations at higher temperatures, and to do them at as low temperatures as possible, *e.g.*, for fluid substances, down to -100°C . These portions of the curve are much more characteristic and permit a surer classification.

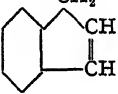
SECTION C. PLASTICS (HIGH MOLECULAR WEIGHT).

THE POLYMERISATION OF HYDROCARBONS.

BY M. W. PERRIN.

It is well known that certain unsaturated hydrocarbons can be converted to true polymers of very high molecular weight. The formation of a hard resin-like product from styrene, for example, was recorded in 1839 while the natural hydrocarbon, rubber, has the same empirical formula as isoprene. All unsaturated hydrocarbons might, in theory, be expected to form similar high molecular weight polymers, but in practice there are great differences in the conditions under which such a reaction will occur for any particular one, and in some cases it has not been found possible to obtain a high molecular weight polymer at all.

TABLE I.

<i>Olefines</i>	Ethylene	$\text{CH}_2 = \text{CH}_2$
	<i>Is</i> -Butylene	$\text{CH}_2 = \text{C}(\text{CH}_3)_2$
	Styrene	$\text{CH}_2 = \text{CH} \cdot \text{C}_6\text{H}_5$
	Indene	
<i>Diolefines</i>	Butadiene — 1, 3	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
	Isoprene	$\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CH} = \text{CH}_2$
	2-Phenyl Butadiene — 1, 3	$\text{CH}_2 = \text{C}(\text{C}_6\text{H}_5) - \text{CH} = \text{CH}_2$
	<i>p</i> -Divinyl benzene	$\text{CH}_2 = \text{CH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH} = \text{CH}_2$
<i>Acetylene Series</i>	Acetylene	$\text{CH} \equiv \text{CH}$
	Vinyl Acetylene	$\text{CH} \equiv \text{C} - \text{CH} = \text{CH}_2$
	Divinyl Acetylene	$\text{CH}_2 = \text{CH} - \text{C} \equiv \text{C} - \text{CH} = \text{CH}_2$

If polymers are obtained from the simple olefines, containing one unsaturated bond, they will generally be of the long-chain type, while those obtained from diolefines or from hydrocarbons of the acetylene series may have a more complex three-dimensional structure which is produced through the branching of growing chains or the formation of normal valency links between the large molecules. Apart from the differences in mechanical properties due to these different types of molecular structure, there are also appreciable differences between polymers which have the same general type of structure. All hydrocarbon polymers are excellent electrical insulators and have good water resistance and chemical inertness in accordance with their chemical constitution, but the differences in their mechanical properties, which are due to their different molecular structure, largely determine the uses to which they may be put.

The extensive experimental work dealing with the polymerisation of hydrocarbons cannot be summarised in the present paper, which is only

intended to compare and contrast the behaviour of certain hydrocarbons on polymerisation. Detailed references are to be found in the recent collection of data by Burk, Thompson, Weith and Williams.¹

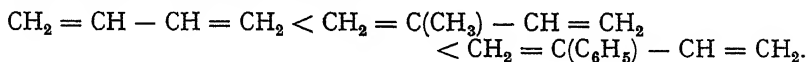
The compounds which have been selected for discussion are listed in Table I.

Formation of Polymers.

The mechanism of polymerisation has been studied most fully in the case of styrene, and the experimental results are in general agreement with a chain growth process in which three independent reactions are involved.² These correspond to the formation of active centres, the growth of large molecules by collisions between an active centre and other monomer molecules, and the deactivation of the growing chains. With certain assumptions as to their kinetic order, measurements of the rate of polymerisation, of the mean molecular weight and of the molecular weight distribution in the product, have been used to calculate the values of the velocity constants and the activation energies for the separate reactions. The activation energy for the chain initiation reaction is about 23,000 cal./mol. and is much greater than that for the chain growth reaction for which a value of about 5700 cal./mol. is found.³ The activation energy of the chain-stopping reaction is intermediate between these two values.

If k_1 , k_2 and k_3 are the velocity constants of the initiation, growth and chain-stopping reactions respectively, the mean molecular weight of the polymer is approximately given by k_2/k_3 and the measured velocity constant of the polymerisation reaction by k_1k_2/k_3 . Increase in temperature will, in general, lead to a faster rate of reaction, but polymers of lower molecular weight will be formed. Dostal, Mark and Raff,⁴ on the basis of this kinetic interpretation, have explained the behaviour of ethylene and of indene, which normally do not form such high molecular weight polymers as styrene, as being due to the much higher activation energy for the primary process in the case of these two compounds. In the thermal dimerisation of ethylene, Storch has obtained a value of 42,000 cal./mol. for the activation energy.⁵ Because of this, a higher temperature is necessary for the reaction to have a measurable rate and, under these different conditions, the chain-stopping mechanism may well be taking place more rapidly compared with the growth process, so that only low molecular weight polymers are obtained.

The values of the activation energies of the separate reactions involved during polymerisation will be affected by the chemical nature of groups near the initial unsaturated bond in the molecule. The effect of such groups on the rate of polymerisation has been clearly shown by Whitby and co-workers⁶ who have studied, under comparative conditions, a large number of substituted 1, 3-diolefines. The rate of polymerisation increases, for example, in the series :



¹ R. E. Burk, H. E. Thompson, A. J. Weith, I. Williams, *Polymerisation*, A.C.S. Monograph Series, New York, 1937.

² Cf. H. Staudinger, *Die Hoch-molekularen Organischen Verbindungen*, Berlin, 1932.

³ G. V. Schulz, E. Husemann, *Z. physik. Chem., B*, 1936, **34**, 187.

⁴ H. Dostal, H. Mark, R. Raff, *Ind. Eng. Chem.*, 1937, **29**, 595.

⁵ H. Storch, *J.A.C.S.*, 1934, **56**, 374.

⁶ G. S. Whitby, R. N. Crozier, *Can. J. Res.*, 1932, **6**, 203.

The nature of the substituent group may also influence the degree of polymerisation and, in the above compounds, the 2-phenyl derivative only gives low molecular weight products, while butadiene and isoprene readily form high polymers. In this connection consideration must be given to the possible effect of steric hindrance, due to the size of the substituent groups, in preventing the formation of a high polymer.

While the principle of a chain mechanism for polymerisation is generally accepted, many possibilities are still open in describing the detailed mechanism of the reaction. The initiation of an active centre may result from a bimolecular collision with the necessary thermal energy or from a photo-chemical activation, while the stopping mechanism may vary from the simplest case, in which all the monomer is used up, to more complicated mechanisms such as collision with a wall or foreign molecule; collision of a different sort with a monomer; collision of two growing chains; or redistribution of excess energy in the growing chain itself, either by ring closure or some other mechanism. Largely due to the work of Staudinger, the actual chain growth is generally considered to take place as a result of successive collisions between monomer molecules and a free radical formed in the initiation process. It is, however, also possible that the process of growth should be considered as a series of normal bimolecular reactions between monomer molecules and an initial activated molecule in the course of which a hydrogen atom is transferred along the chain after each effective collision, so as to form a new unsaturated bond ready, and still in an activated state, for the next addition. If this mechanism is correct it is reasonable to suppose that the value of the bimolecular velocity constant will be largely controlled by the temperature independent factor, α , in the Arrhenius equation, $k = Z\alpha e^{-E/RT}$, for reaction velocity. The numerical value of α will probably decrease as the size of the molecule becomes greater.

The polymerisation of hydrocarbons is very sensitive to the influence of catalysts. Such catalysts may be of various chemical types, of which the best known are oxygen and unstable peroxides such as benzoyl peroxide. When present, even in very small amounts, they increase the rate of polymerisation, and also lower the mean molecular weight of the polymer. The method by which these catalysts act is not fully understood, but is probably through the formation of some unstable oxidation product of the unsaturated monomer, the decomposition of which provides the free radical or activated molecule necessary to start the chain growth. Such intermediate oxidation products, however, have not yet been isolated, and their constitution still lacks definite proof. The catalytic effect of alkali metals, and particularly of sodium, on the polymerisation of butadiene has been the subject of much experimental work, and is used in practice in the manufacture of a Russian "synthetic rubber." Inorganic halides such as $AlCl_3$ or BF_3 are also important polymerisation catalysts and the latter is used, at temperatures below $-10^\circ C$. in the preparation of a high molecular weight polymer of *iso*-butylene.⁷

External variables are of great importance in polymerisation reactions though relatively little experimental data, except in the case of temperature variations, is as yet available. Dostal, Mark and Raff⁴ have shown that the rate of polymerisation of styrene in toluene solution decreases as the dilution is increased, and there is also experimental

⁷ Brit. Pat. 401,297.

evidence that the molecular weight is lower under these conditions. Schulz and Husemann⁸ found a linear relationship between the mean molecular weight and the square root of the styrene concentration, while Suess, Pilch and Rudorfer⁹ found that, at low concentrations, the molecular weight was proportional to the concentration. Polymerisation reactions are, in practice, often carried out with the monomer in the form of a dispersion or emulsion in some non-solvent, and under these conditions the effects both of surface forces and of the different rate of removal of the reaction heat may give rise to appreciable changes in the velocity and the degree of polymerisation.

These reactions are also particularly sensitive to high pressure which produces larger effects than can be accounted for only in terms of the decrease in volume which normally occurs on polymerisation. It is probable that the influence of a high hydrostatic pressure on the duration of molecular collisions in condensed systems must be taken into account. Conant and Tongberg¹⁰ have studied the rate of polymerisation of isoprene at room temperature under pressures up to 12,000 atmospheres. Although the individual results varied widely according to the history of the sample used, the figures in Table II for the ratio of the velocity constants at different pressures show the large increase in rate which was obtained. The values of k were calculated from the equation

$$k = \frac{2.3}{t} \log \frac{1}{1-Z},$$

where t is the time and Z the fraction polymerised. Increases in the rate of polymerisation with pressure for other hydrocarbons have also been found by Tammann and Pape and by Sapiro, Linstead and Newitt. In addition to this effect it has also been found¹¹ that under a sufficiently high pressure, which must be at least 1200 atmospheres if no oxygen is present or at least 500 atmospheres if there is a small proportion of free oxygen, ethylene will form a high molecular weight polymer which is a solid under normal conditions.

TABLE II.

$\frac{k(12,000)}{k(9,000)} = 3.5$
$\frac{k(12,000)}{k(6,000)} = 17; 30$
$\frac{k(12,000)}{k(2,000)} = ca. 100$

Properties of Polymers.

One of the most important differences in the properties of hydrocarbon polymers is due to the type of molecular structure involved. This is well illustrated by comparison of the polymers of acetylene and ethylene. The former is converted to a solid polymer when bombarded by α -particles from radon and the work of Mund and Koch and of Lind and Bardwell has shown that approximately 20 molecules of monomer react for every ion-pair produced in the gas.¹² Although the polymer thus has a relatively low molecular weight it is insoluble and, on heating, decomposes without melting. The solid polymer of ethylene, on the other hand, has a much higher molecular weight but is soluble when heated in hydrocarbon solvents and can be melted reversibly. The difference in behaviour can be accounted for by the fact that acetylene, with

⁸ G. V. Schulz, E. Husemann, *Z. physik. Chem.*, B, 1937, 36, 184.

⁹ H. Suess, K. Pilch, H. Rudorfer, *Z. physik. Chem.*, 1937, 179, 36.

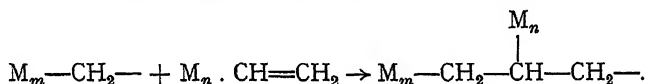
¹⁰ J. B. Conant, C. O. Tongberg, *J.A.C.S.*, 1930, 52, 1659.

¹¹ Brit. Pat. 471,590.

¹² S. C. Lind, *The Chemical Effects of α -Particles*, A.C.S. Monograph Series, New York, 1928.

its triple bond, will form a three-dimensional molecular network, while the ethylene polymer molecules are long chains unconnected with each other. The addition of *p*-divinyl benzene to styrene in amounts as small as 0.01-0.002 per cent. has been shown by Staudinger¹³ to have a great effect on the properties of the polymer which is no longer soluble but instead, swells to many times its original volume. The two double-bonds in *p*-divinyl benzene are, in this case, used to form bridges between the growing styrene chains. Similar cross-linked molecular structures are also readily obtained from vinyl acetylene and di-vinyl acetylene.¹⁴

While the polymerisation of butadiene normally leads to the formation of straight chains as a result of 1-4 addition it is possible with this compound, and with other diolefines, to obtain both three-dimensional structures and branched chains. There is also some evidence that, under certain experimental conditions, branched chain polymers can be obtained with the simple olefines and, in order to explain this, Flory¹⁵ has suggested that reaction may take place between a growing chain and another polymer molecule according to the scheme:—



The hydrocarbon polymers which have a simple chain structure are particularly characterised by their elastic properties, and in this respect they show the greatest difference in behaviour from ordinary low molecular weight solids. With the latter there is a range in which an applied stress will cause a small reversible elastic deformation, but with the high molecular weight compounds a reversible elastic deformation is obtained which may reach a value of several hundred per cent. The best known example of this behaviour is, of course, the natural polymer rubber, but it is also shown by the normally brittle polymers of styrene in a higher temperature range. Not only is the extent of elastic deformation very large, but a more fundamental difference is found in that the elasticity modulus for these polymers increases, while that of normal solids decreases, with increase in temperature.

Many theories have been advanced to account for this behaviour of rubber and other long chain molecules, including an explanation based on the flexibility and length of the chains which is due to Guth and Mark.¹⁶ If the polymer chains are sufficiently long they can exist in a number of more or less coiled configurations without any strain. At any given temperature there will be a statistical distribution of configurations, the most probable value of which will not correspond to the chains being straight. When such a material is stretched the chains will be straightened and an arrangement of greater order will be formed with a consequent decrease in the entropy of the system. The increase in length on stretching is thus analogous to the decrease in volume of an ideal gas on compression and, if carried out adiabatically, will result in both cases in an increase in temperature. Equations similar in form to the gas laws have been developed to cover the simplest picture and these can be refined, along the lines of the van der Waals' equation of state, by taking into account the resistance to free rotation (due, for example, to sub-

¹³ H. Staudinger, *Trans. Faraday Soc.*, 1936, **32**, 323.

¹⁴ R. G. W. Norrish, E. F. Brookman, *Proc. Roy. Soc., A*, 1937, **163**, 205.

¹⁵ P. J. Flory, *J.A.C.S.*, 1937, **59**, 241.

¹⁶ E. Guth, H. Mark, *Mh. Chem.*, 1934, **65**, 93.

stituent groups or the presence of double bonds in the chain) and the possibility of forming an ordered crystalline state of lower energy. This last possibility is analogous to the condensation of a real gas at a definite pressure below the critical temperature, and is associated with the evolution of a definite latent heat.

The behaviour of rubber, which is normally amorphous but develops a crystalline fibre structure when stretched, is well known, and it is of interest to compare the polymers of styrene and of ethylene. The former is amorphous while the latter, due possibly to the very simple structure of the molecules, is a well-defined crystalline material.

Summary.

The behaviour of certain unsaturated hydrocarbons on polymerisation is compared, and the differences are discussed in terms of the various factors involved in this type of reaction.

The properties of certain high molecular weight polymers and their relationship with the molecular structure are also described. The mechanical and thermal behaviour depend on the existence of a three-dimensional or two-dimensional structure, while differences in the elastic properties of the long chain polymers are due to the detailed constitution of the molecules.

*Imperial Chemical Industries, Ltd.,
London.*

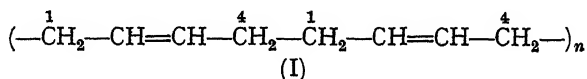
BUTADIENE POLYMERS; ELUCIDATION OF STRUCTURE BY OZONOLYSIS.

BY R. HILL, J. R. LEWIS AND J. L. SIMONSEN.

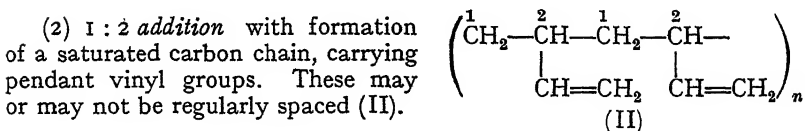
Received 1st March, 1939.

Butadiene can polymerise by three primary mechanisms:—

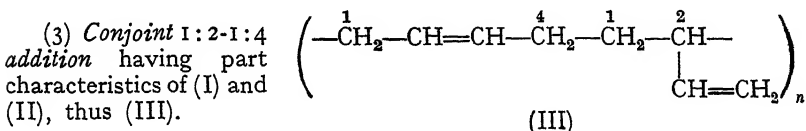
(1) 1:4 *addition* to give a straight chain unsaturated hydrocarbon
(I):—



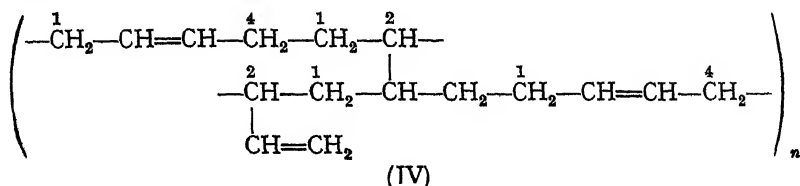
(2) 1:2 *addition* with formation of a saturated carbon chain, carrying pendant vinyl groups. These may or may not be regularly spaced (II).



(3) *Conjoint* 1:2-1:4 *addition* having part characteristics of (I) and (II), thus (III).



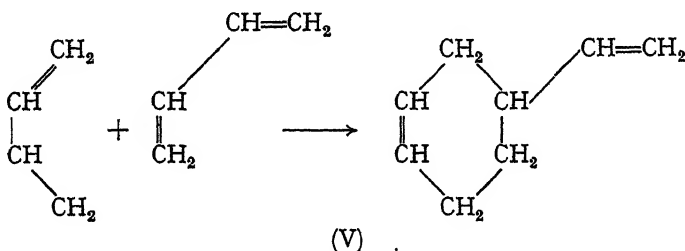
In the case of II and III, chain branching may occur, for example (IV) :—



When account is taken of the possible variation in chain length and molecular weight distribution, it will be apparent that the properties of butadiene polymers can vary widely according to the underlying mechanism and environment of polymerisation.

Various methods have been employed to bring about the polymerisation of butadiene. Thermal polymerisation at elevated temperatures either in the liquid or gas phase results in variable amounts of dimer and polymer; at high temperatures, polymer formation is excluded.^{1, 2, 3, 4, 5, 6}

It is now generally agreed that the dimer is vinyl Δ^3 -cyclohexene (V)—(cf. III) :—



Photopolymerisation in the liquid⁷ and gaseous phase⁸ have recently been studied, but nothing is known concerning the structure of the polymers except that the gas phase photopolymer is probably cross-linked in view of its non-swelling nature.

Polymerisation in the liquid phase by means of metallic sodium has been known for many years.

The classical researches of Harries⁹ on the ozonolysis of natural and synthetic rubber, led early to a broad distinction between two types of synthetic rubber. The products formed by 1:4-addition of dienes were regarded as being analogous to natural rubber in constitution and were termed "normal" since they both gave essentially 1:4-dicarbonyl compounds on ozonolysis. The rubbers which gave other decomposition products were classed as "abnormal." In general, Harries found that when dienes were polymerised by heating 8-24 days at 100-110° C., or

¹ Hoffmann and Tank, *Z. angew. Chem.*, 1912, **25**, 1465.

² Lebedev *et al.*, *Sintet Kaut.*, 1936, **5**, No. 1, 2.

³ Vaughan, *J. Am. Chem. Soc.*, 1932, **54**, 3863.

⁴ Lebedev, *J. Phys. Chem. Soc. U.S.S.R.*, 1919, **45**, 1924.

⁵ Moor, Stigaleva, Schiljaeva, *J. Gen. Chem. U.S.S.R.*, 1935, **5**, 818.

⁶ Lebedev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1313.

⁷ Kublicki, *Sintet. Kaut.*, 1936, **5**, 30.

⁸ Gee, *Trans. Faraday Soc.*, 1938, **34**, 712.

⁹ *Untersuchungen über die natürlichen and kunsilichen Kautscharten*, Berlin, 1919.

4-6 weeks at 60° C., "normal" rubbers were obtained. In the case of butadiene however, this conclusion is open to doubt, since the yield of ozonide was poor, and the amounts of succinic dialdehyde and succinic acid isolated were low. On the other hand, the sodium catalysed butadiene polymers were classed as "abnormal." These polymers formed fairly stable ozonides, the only identifiable product isolated in low yield being glyoxal.

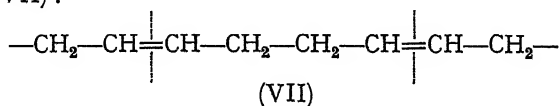
More recently, Pummerer¹⁰ has made a more detailed study of sodium catalysed butadiene polymers. Ozonolysis proceeded slowly, and it was by no means certain that all the double bonds present had been attacked. Decomposition of the ozonide gave 80 per cent. of the carbon skeleton as a white powder having the characteristics of a high polymer, which appeared to be a polymeric aldehyde-acid with the aldehyde groups somewhat in excess (VI). A small amount of succinic acid was also isolated. This led to the view that the sodium catalysed butadiene polymers are formed by conjoint 1 : 2-1 : 4 addition with, it would appear, 1 : 2 addition predominating.

It has been of interest to compare briefly the polymerisation of butadiene in aqueous emulsion with the other methods mentioned, and to ascertain as far as possible the structure of a polymer formed in this manner.

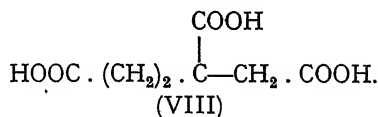
In order to effect polymerisation in aqueous emulsion no added catalyst is necessary. It is at once immediately obvious that polymerisation progresses more rapidly in this environment than by the methods already mentioned, and it is assumed that differences in the chain initiation, propagation and termination mechanisms are responsible for this. The emulsion butadiene polymer is evidently cross-linked judged from its behaviour towards organic solvents. It has been subjected to ozonolysis, and the products resulting from the degradation of the ozonide examined. The method employed was to remove volatile aldehydes in steam, oxidise the non-volatile residue, isolate the resulting acids, esterify, and separate the methyl esters by fractionation.

In common with Pummerer¹⁰ it has not been possible to account completely for the carbon skeleton originally present. The following have been isolated from degradation of the ozonide :—

1. Succinic acid and succindialdehyde (isolated as dimethyl ester and 2 : 4-dinitrophenylhydrazone respectively). These result from 1 : 4 addition thus (VII) :—



2. Butane-1-2-4-tricarboxylic acid (VIII) (isolated as trimethyl ester) :—

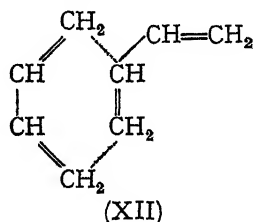


¹⁰ Pummerer, *Kaut.*, 1934, 10, 149.

lower addition products favour a 1:4-activation, the formation of high molecular weight products by this mechanism has not been substantiated.

The factors responsible for polymerisation in aqueous emulsion are as yet imperfectly understood. The following tentative theory however, accounts for the observed facts and receives striking support from the observations recorded in the following communication. The chain initiation mechanism may be conceived as a dimerisation of butadiene in which the orienting forces at the interface maintain the open chain activated dimer in this condition sufficiently long for chain growth to commence as shown in No. XI, p. 1070.

Assuming that the molecular weight of this polymer is great as seems probable, then it will be apparent that quite a slow initiation rate will be sufficient to bring about a rapid polymerisation. Thus it seems possible that the thermal dimerisation, may in the particular environment under consideration be responsible for promoting chain initiation. There probably exists attractive forces between molecules of butadiene which can be represented as a dimer complex, thus (XII).



By comparison with the forces prevailing between butadiene and conjugated mono-olefinic compounds (see following communication), the force existing between two molecules of butadiene will be weak. During the growth of the chain, butadiene may add to the active end(s) either by 1:4 addition, 1:2 addition or as a dimer complex resulting in conjoint 1:2-1:4 addition. Chain branching may occur where 1:2 or 1:2-1:4 addition prevails. In this manner molecules of complex structure are built up. The somewhat indefinite cross-linked structure of butadiene polymers made in aqueous emulsion must be ascribed to the weak polar character of butadiene. In the following communication it is shown how the polymerisation of butadiene can be directed very largely towards a 1:4 mechanism.

Experimental.

1. Polymerisation of Butadiene in Aqueous Emulsion.

Butadiene (230 g.) was charged into a stainless steel autoclave containing water (400 c.c.), dilute acetic acid (22 c.c. of N./1), carbon tetrachloride (80 g.) as polymerisation regulator, and cetyl trimethyl ammonium bromide (8 g.) as emulsifying agent.¹² The resulting emulsion was agitated for 118 hours at 60° C. and the polymer then isolated by coagulation with ethyl alcohol. The coagulum was washed repeatedly on a rubber roller mill with cold water until free from emulsifying agent, and phenyl β -naphthylamine (3 g.) added as antioxidant. The resulting polymer (182 g.) formed a weak crumb-like sheet. It was substantially insoluble in benzene, acetone, ethyl acetate, acetic acid and carbon tetrachloride.

2. Ozonolysis of Butadiene Polymer.

The polymer neither dissolved nor swelled appreciably in chloroform. Ozonolysis of a suspension of the polymer (3 g.) in chloroform (100 c.c.) was complete in three days. The combined solvents from the oxidation of 50 g. of polymer were removed under diminished pressure, the ozonide decomposed with hot water and the volatile products removed in steam.

¹² Cf. B.P. 330,272, I.G. 29.12.28.

Half of the steam distillate gave 5.4 g. of a 2:4-dinitrophenylhydrazone insoluble in ethyl acetate and which crystallised from nitrobenzene in needles, and is undoubtedly the bis-2:4-dinitrophenylhydrazone of succindialdehyde, m.p. (decomp.) 265° C. (Found: N, 26.1 per cent. $C_{16}H_{14}O_8N_8$ requires N, 25.1 per cent.).

The aqueous residue from the steam distillation was neutralised with sodium carbonate and extracted with ether. Removal of the ether left no neutral product. Aqueous potassium permanganate (1 per cent.) was gradually added to the alkaline solution, cooled to 0°, until oxidation was complete. The excess potassium permanganate was destroyed by sulphur dioxide, the manganese dioxide filtered and digested several times with water. The combined filtrates were evaporated to dryness, carefully acidified with methyl alcohol-sulphuric acid mixture (1:1), and the liberated acids esterified azeotropically. The esterification mixture contained a considerable amount of resinous acid (10.6 g.) which was

removed by washing with dilute sodium carbonate solution. Repeated attempts to esterify this acid were unsuccessful.

Table I gives the yields of twice fractionated esters.

Fraction 1—was quantitatively hydrolysed to succinic acid.

Fraction 4—was refractionated and the main portion,

b.p. 166-167°/20 mm., analysed (Found: C, 50.8; H, 6.7. $C_{10}H_{10}O_8$ requires C, 51.7; H, 6.9 per cent.). Acid hydrolysis of 4 and 5 yielded a viscous acid which solidified on trituration with ether and crystallised from ether or acetone in prisms, m.p. 116-120° (Found: C, 44.7; H, 5.1; M, 202. $C_7H_{10}O_8$ requires C, 44.2; H, 5.3 per cent.; M, 190). This acid is readily soluble in water and acetone, sparingly so in ether and benzene and is undoubtedly butane-1-2-4-tricarboxylic acid, for which Howarth and King¹³ give m.p. 120°.

Vinyl groups will be degraded to formaldehyde, formic acid or carbon dioxide. No evidence of formaldehyde could be obtained in the steam distillate, although attempts were made to effect a separation of the 2:4-dinitrophenyl-hydrazone by precipitation of fractions of the distillate, and by chromatogenic adsorption methods. Schryver's formaldehyde test also gave negative results.

Carbon dioxide evolved during the decomposition of the ozonide was estimated by absorption in baryta. Formic acid was estimated in the steam distillate by titration, after removal of aldehydes.

Table II summarises the products isolated from 100 g. polymer, based

TABLE I.

1	94-100°/20 mm.	23.7 g.
2	100-150°/20 mm.	3.2 g.
3	150-165°/20 mm.	1.0 g.
4	165-175°/20 mm.	7.8 g.
5	175-190°/20 mm.	1.3 g.
6	Residue	9.2 g.

TABLE II.

	Weight.	(CH ₂).	Butadiene.
1. Dimethyl succinate	51.6	—	19.1
2. Trimethyl butane-1-2-4-carboxylate	22.4	—	10.6
3. Neutral ester residue	18.4	—	18.4
4. Resinous acid	21.2	—	21.2
5. Succindialdehyde (as 2:4-dinitrophenyl-hydrazone)	21.66	—	2.6
6. CO ₂ as BaCO ₃	18.89	1.34	—
7. Formic acid	166 c.c. N.	2.32	—

Weight of polymer accounted for 75.56

¹³ Howarth and King, *J. Chem. Soc.*, 1914, 105, 1350.

on the assumption that the unidentified ester fractions contain equal amounts of the di- and tricarboxylic esters.

Carbon dioxide and formic acid under 6 and 7 cannot be taken as fully representative of vinyl groups since the solvent undergoes some decomposition under the conditions of ozonolysis with formation of phosgene, and secondary reaction may then ensue with formation of some formic acid and possibly carbon dioxide. On this account the above figures must be accepted with considerable reserve. They are omitted from Table III which summarises in final form the results of ozonolysis.

TABLE III.

	Butadiene (%).
1 : 4-addition only (I) .	21.7
1 : 4- and 1 : 2-addition (III) .	10.6
Resinous acid . . .	21.2
Neutral esterification . .	18.4

Summary.

Ozonolysis of a butadiene polymer gave succinic acid, butane-1 : 2 : 4-tricarboxylic acid and resinous acids. These results show that in aqueous emulsion, butadiene polymerises by all the possible additive mechanisms, but a quantitative discrimination between the various mechanisms is not possible. It is suggested that chain initiation is due to the formation of a "dimer complex," which under normal conditions yields vinyl Δ^3 -cyclohexene.

The authors wish to express their thanks to Imperial Chemical Industries (Dyestuffs Group) for a grant and for agreement to the publication of the results of this work.

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BUTADIENE CO-POLYMERS : ELUCIDATION OF STRUCTURE BY OZONOLYSIS.

BY R. HILL, J. R. LEWIS AND J. L. SIMONSEN.

Received 1st March, 1939.

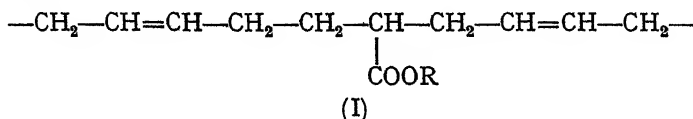
Co-polymerisation is the term applied when two or more unsaturated substances polymerise together. Although many examples of the application of co-polymerisation to the preparation of new synthetic polymers will be found in the technical literature,¹ comparatively little is known of their structure. It was therefore of interest to examine the effects resulting from the co-polymerisation of a second compound with butadiene, since the structure of a butadiene polymer had already been ascertained.

Ziegler² has observed that butadiene is capable of co-polymerising with vinyl compounds such as acrylic esters in aqueous emulsion, with

¹ *The Chemistry of Synthetic Resins*, Carlton Ellis, 1935.

² Ziegler, *Chem. Z.*, 1938, 63, 125.

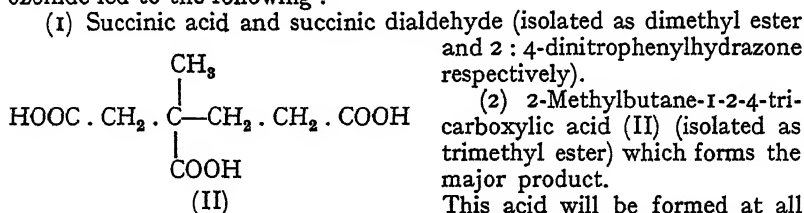
formation of large molecules in which the two components are distributed along the chain, a typical section of which could be represented as follows :—



However, no proof has yet been advanced which establishes beyond doubt a co-polymer structure. Even accepting a co-polymer structure, nothing is known regarding the character of the main carbon chain, and the distribution of the units.

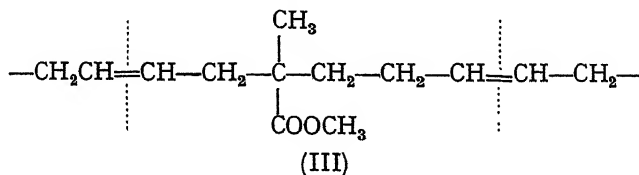
For the purpose of the present investigation, methyl methacrylate was selected as a typical unsaturated compound for co-polymerisation with butadiene. When methyl methacrylate is polymerised alone, it forms a hard tough transparent glass.³ This is a linear polymer of high molecular weight, but the distribution of the pendant groups along the main carbon chain is not known.

Equimolecular quantities of butadiene and methyl methacrylate were polymerised together in aqueous emulsion. Examination of the resulting product showed that both components were still present in equimolecular amount. This product was subjected to ozonolysis, and the ozonide resolved according to the method already described (previous communication). Compared with the butadiene polymer it has been possible to account more completely for the carbon skeleton. The carbon recovery compares favourably with that recorded by Klebansky and Wassiljewa⁴ for 2-chloro-1:3-butadiene polymer, and with the more recent work of Pummerer on natural rubber.^{5, 6} Decomposition of the ozonide led to the following :—



(2) 2-Methylbutane-1-2-4-tricarboxylic acid (II) (isolated as trimethyl ester) which forms the major product.

This acid will be formed at all points in the chain when methyl methacrylate is sandwiched between 2 mols. of butadiene polymerised according to 1:4 addition, thus (III) :—



(3) A tetracarboxylic ester having the composition $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{OMe})_4$; this can be formed either from hexane 2-4-dimethyl-1-2-4-6-tetracarboxylic

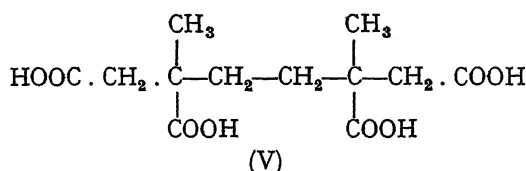
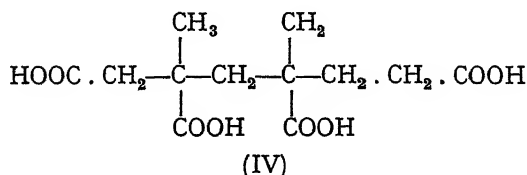
³ Strain, *Ind. Eng. Chem.*, 1938, 30, 345.

⁴ Klebansky and Wassiljewa, *J. Pract. Chem.*, 1936, 144, 251.

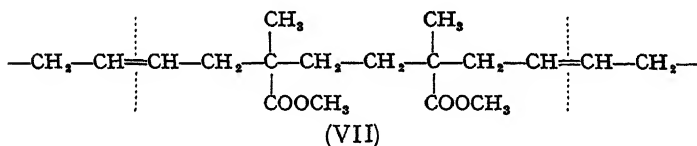
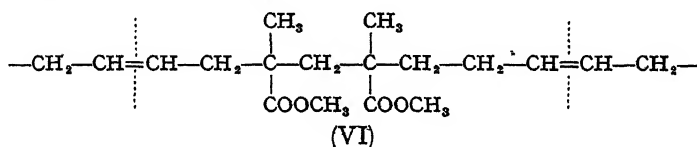
⁵ Pummerer, Erbermayer, and Gerlach, *Ber.*, 1931, 64, 804.

⁶ Pummerer, Matthaus, Socias, and Vinals, *Ber.*, 1936, 68, 170.

acid (IV), or the isomeric hexane 2-5-dimethyl-1-2-5-6-tetracarboxylic acid (V):—

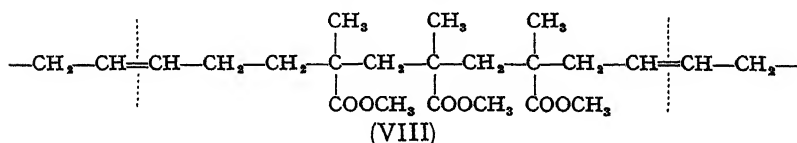


These acids result from sections of the chain where two molecules of methyl methacrylate are adjacent to one another, the particular acid formed depending upon whether the adjoining methyl methacrylate radicles are linked 1 : 2—1 : 2 (VI) or 1 : 2—2 : 1 (VII):—

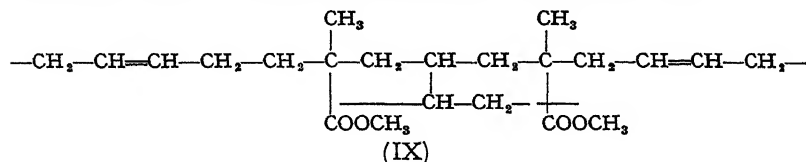


(4) A neutral ester residue.

This is made up of more complicated fragments where for example three or more methyl methacrylate radicles are directly joined (VIII):—



or possibly where 1 : 2 addition of butadiene has occurred (IX):—

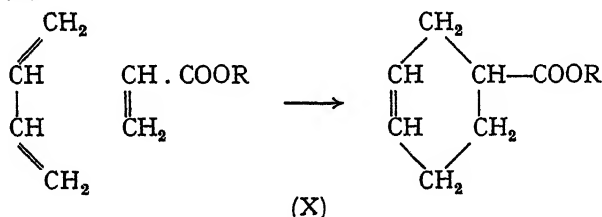


A number of striking features emerge from a consideration of these observations. Considerably more than one-half of the chain is made of alternating butadiene and methyl methacrylate units. The presence of

units consisting of two methyl methacrylate radicals sandwiched between two molecules of butadiene has been established. There are comparatively few points in the chain where butadiene units are immediately adjacent. The butadiene polymerises for the most part by 1 : 4-addition. It is significant that butane-1-2-4-tricarboxylic acid has not been isolated, but it is not possible on the evidence available to discount the possibility of some 1 : 2 addition. The solubility of this co-polymer indicates that comparatively little chain branching has occurred, and it seems probable that the structure is essentially linear. It is thus apparent that butadiene polymerises by a different mechanism, according as to whether methyl methacrylate is present or not. The presence of methyl methacrylate induces a 1 : 4 mechanism. On general grounds it is probable that chain branching will occur to a much less degree under these circumstances, which seems to account at least in part for the poorly developed rubber-like characteristics of the butadiene polymer as compared with the co-polymer.

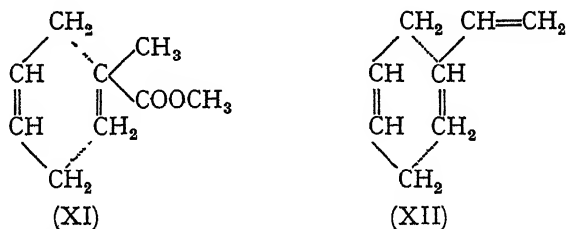
It is clear that the favoured chain propagation reaction is one involving the addition of alternate molecules of butadiene and methyl methacrylate to the active end of the chain. Any theory must take account of this, and also of the effect of the methyl methacrylate in inducing 1 : 4 addition of butadiene.

It is stated that butadiene undergoes a Diels-Alder reaction with acrylic derivatives with formation of carboxy- Δ^3 -cyclohexene derivatives (X) :—



A consideration of published data shows that this type of reaction will take preference over the competing reaction, *viz.*, dimerisation of butadiene to vinyl- Δ^3 -cyclohexene.

As an extension of the theory outlined in the previous communication it is suggested that some of the molecules of butadiene and methyl methacrylate form a Diels-Alder complex, thus (XI) :—



which will take precedence over two molecules of butadiene forming a complex (XII). Chain initiation may then be visualised as involving an activated complex, or possibly the Diels-Alder thermal addition proceeding in an environment which favours chain growth rather than ring closure. Chain propagation involves adding on the complex to the growing end of the chain. The seat of chain growth in an emulsion is

not fully established, but this may well occur at the interface. Further it is possible that interfacial forces would favour the formation of complexes of the type described. This would account for differences referred to by Ziegler² who has noted that co-polymerisation (assumed) does not occur when butadiene and acrylic esters are brought together in concentrated form and heated.

Recently, Melville^{7, 8} has observed that butadiene will function as a chain inhibitor in the vapour phase photochemical polymerisation of methyl acrylate. We are therefore led to the general conclusion that the environment which in turn is responsible for the polymerisation mechanism is capable of determining whether or no co-polymerisation can be realised.

Experimental.

Preparation of the co-Polymer of Butadiene and Methyl Methacrylate in Aqueous Emulsion.

Methyl methacrylate (390 g.) and butadiene (212 g.) were charged into an autoclave containing water (800 g.), dilute acetic acid (44 c.c. of *N*/1) and cetyl *p*-dimethylaminobenzoate methosulphate as emulsifying agent.⁹ After agitating for 118 hours at 60° C., dilute sodium hydroxide (200 c.c. of 2 *N*.) was added, and the emulsion warmed to 45° C. to complete coagulation. The product (583 g.) was washed thoroughly on a rubber roller mill with cold water, and phenyl β -naphthylamine (12 g.) added as anti-oxidant. It was tough and rubberlike, this being particularly marked at elevated temperatures. It dissolved slowly in benzene forming a viscous solution.

Ozonolysis of Butadiene-Methyl Methacrylate co-Polymer.

The interpolymer dissolved slowly in chloroform and carbon tetrachloride. A solution of the polymer (3 g.) in chloroform (100 c.c.) required 48 hours for complete oxidation, indicated by stability to bromine. The experimental procedure adopted was similar to that used in the case of the butadiene polymer. From the oxidation of 48 g. of interpolymer, extraction with ether gave a non-ketonic viscous gum (9.0 g.) which for calculation purposes is considered as unoxidised polymer.

The steam distillate yielded 2.6 g. of 2:4-dinitrophenylhydrazone insoluble in ethyl acetate. The carbon dioxide and formic acid isolated is equivalent to 4.6 per cent. methylene groups in the polymer, but for reasons, outlined in the previous paper, are omitted from the calculation.

Table I condenses the results of two fractionations of the methyl esters obtained from the ozonolysis.

Fraction 1 is composed of approximately equal amounts of dimethyl succinate and trimethyl 2-methylbutane-1 : 2 : 4-tricarboxylate since it yields on acid hydrolysis succinic acid and the impure tricarboxylic acid.

Fraction 2. B.p. 154-160°/20 mm. Found: C, 53.1; H, 7.3. $C_{11}H_{18}O_6$ requires C, 53.7; H, 7.3 per cent.

TABLE I.

1	80-150°/15 mm.	4.0 g.
2	150-175°/15 mm.	21.0 g.
3	130-145°/3 mm.	4.0 g.
4	145-180°/3 mm.	7.0 g.
5	Residue	11.4 g.

⁷ Melville, *Proc. Roy. Soc.*, 1938, 167, 99.

⁸ Melville, *Proc. Rubber Tech. Conf.*, 1938, 239.

⁹ Cf. B.P. 485,941, I.C.I., 25.8.36.

Acid hydrolysis of Fractions 2 and 3 yielded an acid which crystallised from hydrochloric acid in rectangular plates, m.p. 84-89°, both alone and in admixture with a synthetic specimen of 2-methylbutane-1:2:4-tricarboxylic acid (Found: C, 45.2; H, 6.0. $C_8H_{12}O_6$, $\frac{1}{3}H_2O$ requires C, 45.1; H, 6.1 per cent.). The synthetic acid m.p. 85-91° (Found: C, 45.2; H, 6.1, $C_8H_{12}O_6$, $\frac{1}{3}H_2O$ requires C, 45.1; H, 6.1 per cent.) was obtained by acid hydrolysis of the ethyl ester, described by Ruzicka.¹⁰ The anhydrous acid crystallised from ether-benzene in cubes, decomp. 104° (Found: C, 47.1; H, 6.3. $C_8H_{12}O_6$ requires C, 47.0; H, 5.9 per cent.), but a change in composition and m.p. indicates that it hydrates slowly on exposure to the air.

Analyses of successive fractions, obtained on redistillation of fraction 4, indicated the amount of tetracarboxylic ester increased with b.p. (Found for a fraction b.p. 190-205°/3 mm. C, 55.5; H, 7.3; OMe, 30.3. $C_{12}H_{14}O_4$ (OMe)₄ requires C, 55.5; H, 7.5; OMe, 35.8 per cent.). Acid hydrolysis of this analytical specimen gave a viscid acid, which could not be characterised.

Table II summarises the product isolated from 100 g. of interpolymer.

TABLE II.

	Weight.	(CH ₂).	Butadiene.	Methyl Methacrylate.	Total.
1. Dimethyl succinate .	5.64	—	2.09	—	2.09
2. 2-Methylbutane-1:2:4-tricarboxylic ester .	78.73	—	17.29	32.01	49.30
3. Tetracarboxylic ester .	8.97	—	1.40	5.19	6.59
4. Neutral ester residue .	29.23	—	3.54	19.67	23.21
5. Succindialdehyde (as (2:4-dinitrophenylhydrazone) .	13.33	—	1.61	—	1.61
6. CO ₂ as BaCO ₃ .	16.66	1.18	—	—	1.18
7. Formic acid .	247 c.c. N.	3.46	—	—	3.46

Weight of polymer accounted for = 87.44 g.

These values are based on the assumption that the unidentified ester fractions contain equal amounts of the nearest identified esters and that the residue consists of a pentacarboxylic ester, such as would result from a chain (VIII). For reasons, already outlined in the previous paper, 6 and 7, are omitted from Table III, which summarises in final form the results of the ozonolysis.

TABLE III.

	Weight of Unit.	Butadiene.	Methyl Methacrylate.
Butadiene units .	3.7	3.70	—
Butadiene-methyl methacrylate (1:1) .	49.30	17.29	32.01
Butadiene-methyl methacrylate (1:2) .	6.59	1.40	5.19
Neutral ester residue (assuming butadiene-methyl methacrylate 1:3) .	23.21	3.54	19.67
Total.	82.80	25.93	56.87

The interpolymer contains 64 per cent. of methyl methacrylate and 34 per cent. of butadiene. The greater loss in calculation of the butadiene content may be due to omission of the methylene groups.

Summary.

Isolation of 2-methyl-1:2:4-tricarboxylic acid, from the ozonolysis of a product obtained by polymerising equimolecular quantities of butadiene and methyl methacrylate together in aqueous emulsion establishes a co-polymer structure. More than half of the essentially linear polymer is composed of alternate units of butadiene and methyl methacrylate. In this case, butadiene polymerises in the main by 1:4-addition. An extension of the "activated complex" theory, suggested in the previous communication, correlates the differences in structure and properties between the co-polymer and the butadiene polymer, prepared under comparable conditions.

The authors wish to express their thanks to Imperial Chemical Industries (Dyestuffs Group) for a grant and for agreement to the publication of the results of this work.

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University College of North Wales,
Bangor.

GENERAL DISCUSSION.*

Prof. R. G. W. Norrish (Cambridge) said: I should like to put before you some recent results which bear on the mechanism of polymerisation of olefinic hydrocarbons. These will be published shortly in the *Proceedings of the Royal Society*.† Many authors, including Staudinger,¹ Mark,² Chalmers,³ and others have hitherto inclined to the view that of the three reactions, initiation, propagation, and deactivation, it is the first which controls the speed of polymerisation of a vinyl compound. According to this view, centres are formed slowly, while chain propagation is extremely rapid, the chain being completed in a fraction of a second. This conclusion is based partly on the results of Staudinger¹ and of Schultz and Husemann⁴ with styrene in which it was found that the average molecular weight is independent of the percentage polymerisation.

The results which I shall describe, indicate, so far as styrene and methyl methacrylate are concerned, a fundamental change in this point of view, in that the reaction of propagation rather than initiation is indicated as the limiting factor, while the molecular weight is a function of the degree of polymerisation. This falls partly into line so far as kinetics are concerned with views previously expressed by Whitby.⁵ This work was done in collaboration with E. F. Brookman.

The polymerisations were carried out with the pure liquid monomers between the temperature of 80° and 120° C. The degree of polymerisation was measured by dissolving the partly polymerised specimen in a suitable solvent, precipitating the polymer by throwing the solution into methyl alcohol, drying and weighing.

* On the three preceding papers.

† *Proc. Roy. Soc., A*, 1939, **171**, 147.

¹ Staudinger, *Trans. Faraday Soc.*, 1926, **32**, 97.

² Dostal and Mark, *ibid.*, 1936, **32**, 54.

³ Chalmers, *J.A.C.S.*, 1934, **56**, 912.

⁴ Schultz and Husemann, *Z. physik. Chem., B*, 1936, **34**, 187.

⁵ Whitby, *Trans. Faraday Soc.*, 1936, **32**, 315.

It was found that with purified methyl methacrylate and styrene the results were irreproducible, and that velocities decreased to extremely low values. With controlled amounts of catalyst,—benzoyl peroxide or methyl methacrylate ozonide—however, they became readily reproducible. It is therefore concluded that a catalyst is always required to start chains.

Under such circumstances the reaction of polymerisation in styrene is of zero order, and with methyl methacrylate it is of zero order until the reaction has proceeded about 20 per cent., after which the medium becomes self-heating due to the impossibility of evacuating the high reaction heat to the thermostat when the convection currents are suppressed by increased viscosity.

We conclude from this reproducibility that a fixed amount of catalyst is responsible for the starting of a fixed number of reaction centres, and that since the reactions are of zero order this number is preserved throughout the whole process of polymerisation. For this to be the case, it is necessary that every time a reaction centre is destroyed, a fresh one should be created.

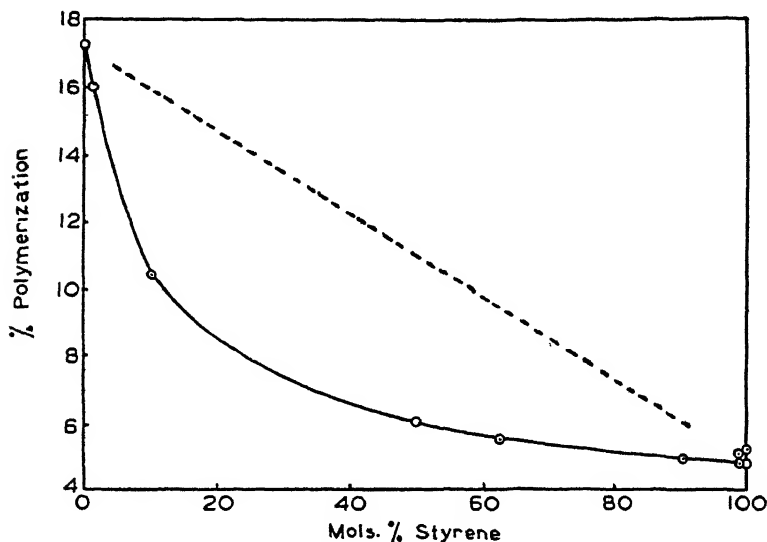


FIG. 1.—Co-polymerisation of methyl methacrylate and styrene with 0.0114 mols. per cent. of benzoyl peroxide as catalyst at 90° C.

The velocity of co-polymerisation of methyl methacrylate and styrene in the presence of benzoyl peroxide as catalyst is dependent on the composition of the binary mixture in a peculiar way. This is shown in Fig. 1 where it is seen that the velocity of polymerisation of methyl methacrylate is markedly depressed by the addition of styrene, being reduced by 50 per cent. by the addition of only 10 per cent. of styrene. If chain starting were here the controlling reaction, and the respective monomeric vinyl compounds entered indiscriminately into the reaction chain, that centre which was most easily formed would be produced, and we should get a relation in which the velocity varied nearly linearly with composition, as shown by the dotted line in Fig. 1. If, however, chain propagation were the limiting factor the velocity would be controlled by four velocity coefficients since there are two kinds of monomer, and two kinds of end to the growing chain (reaction centres). If M be the percentage molar concentration of methyl methacrylate and S that of styrene, so that $M + S = 100$, and if n_1 and n_2 represents the number of the two types of

reaction centre so that in accordance with the principle adumbrated above

$$n = n_1 + n_2 = \text{const.}$$

then the rate of polymerisation is given by

$$dp/dt = k_1 n_1 M + k_1' n_1 S + k_2 n_2 M + k_2' n_2 S$$

combining these two equations with that representing the stationary state of the two types of centre

$$dn_2/dt = k_1' n_1 S - k_2 n_2 M = 0$$

we obtain

$$\frac{dp}{dt} = \frac{a + bS + cS^2}{1 + dS}$$

where a , b , c and d are constants.

By a suitable choice of constants the curve of co-polymerisation can be represented with accuracy. For the curve shown in the figure, which applies to 0.0114 mols. per cent. of the benzoyl peroxide as catalyst at 90° C., the value of c is nearly negligible and the rate of polymerisation is represented accurately by

$$\frac{dp}{dt} = \frac{17.2 + 0.25S + 6.7 \times 10^{-5}S^2}{1 + 0.079S}.$$

It is important to emphasise that a mechanism in which the rate of polymerisation is controlled by chain initiation could not give rise to the kinetic results here outlined. They are only explained if the rate of propagation be the controlling factor. We have found similar marked decreases in the velocity of polymerisation of methyl methacrylate and styrene when they are copolymerised with small quantities of divinyl substance, and have been able to explain the results in a similar way.

These conclusions suggest that the molecular weight may be expected to be a function of the degree of polymerisation, and confirmation of this was obtained both for styrene and methyl methacrylate by the measurement of the specific viscosity of solutions of the polymers separated at various stages of the reactions. The curves shown in Fig. 2 represent the results. According to the equation of Staudinger¹ the quantity η_{sp}/C —which represents the quotient of the specific viscosity and the concentration of the polymer represented as monomer—is a direct measure of the molecular weight of the polymer; in the case of methyl methacrylate it is seen to increase steadily with the percentage polymerisation. With styrene it first increases and then remains constant.

If the number of centres n be represented as a function of the concentration of catalyst

$$n = f(c)$$

and if the destruction of every centre is accompanied by the generation of a new one so that n is constant, and if k and E be the velocity coefficient and energy of activation of the propagation reaction, and q and E' the corresponding quantities for the reaction destroying centres, then the molecular weight M of the polymer will be related to the percentage polymerisation α by the expression

$$M = \frac{\alpha}{f(c) + \frac{q\alpha}{k} e^{-\frac{E'-E}{RT}}}$$

This expression includes all cases.

(1) If $c = 0$ or if c is very small (*i.e.*, absence of catalyst) $M = \text{const.}$ at constant temperature.

This corresponds to the result of Staudinger and Schultz and Husemann⁴ with pure styrene. The molecular weight also decreases with temperature since $E' > E$.

(2) If c is large, and q small, *i.e.*, the chains once started persist, and very few are broken,

$$M = \frac{\alpha}{f(c)}.$$

The molecular weight is then proportional to the percentage polymerisation and varies inversely as the function of the concentration of the catalyst, which may be simply the first power or the square root of the concentration. This corresponds to the results with methyl methacrylate.

(3) The intermediate case between (1) and (2) gives a molecular weight which first grows with percentage polymerisation and finally becomes

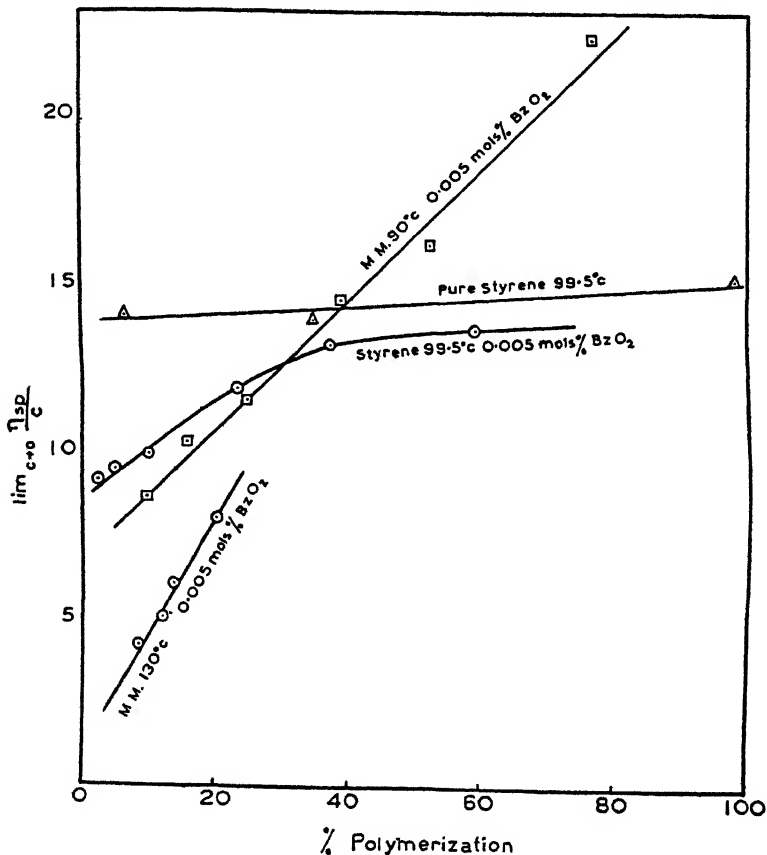
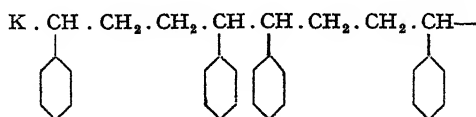


Fig. 2.—Curves showing variation of molecular weight of methyl methacrylate and styrene during the process of polymerisation.

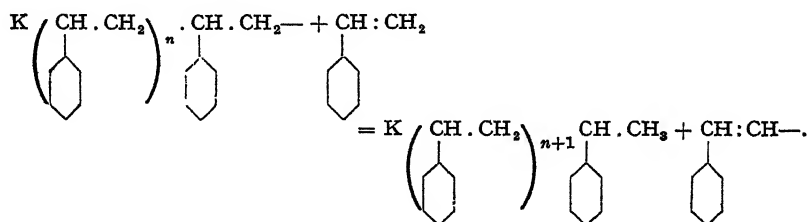
constant, as has been found to be the case with styrene in the presence of catalysts. In such cases the chains grow to a fixed average length. They are then replaced by new centres which grow to the fixed length and in their turn give rise to new centres and so on.

All these kinetic requirements may be visualised in a simple manner by a modification of the mechanism first proposed by Staudinger.¹ We shall assume that the catalyst, either by its decomposition to give a free radical (benzoyl peroxide is a possible source of phenyl radical) or by its reaction with the monomer, starts a reaction centre containing a free

valence. To this reaction centre, molecules of monomeric vinyl compound add themselves successively to build up a polymerised chain, in which the free valence is always preserved at the growing end, *e.g.*,



This reaction of addition of molecules of monomer is to be identified with the limiting factor controlling the reaction velocity. But besides this reaction another of lower probability exists—namely, that of hydrogenation. I have already indicated previously in this discussion⁶ how free hydrocarbon radicals may hydrogenate themselves at the expense of a hydrocarbon solvent. If this occurs here, the growth of the chain will be stopped, but as a new free monomeric radical will be formed, a new centre will be generated :



From this a fresh chain can grow. By the exclusive operation of this mechanism the number of chains is preserved constant and the reaction of zero order. It may be supposed that only in solution where this hydrogenation process is not possible, or in the vapour phase, will the chain length be controlled by the mutual neutralisation of reaction centers.

Thus by a modification of Staudinger's mechanism we may take account of these new facts in the kinetics, and reconcile in a simple way apparently conflicting observations of growth of molecular weight during polymerisation.

While there seems to be in these results the basis of a general theory of the mechanism of the polymerisation of vinyl compounds it would be rash to generalise prematurely. We are, however, carrying out further measurements with other substances to find out how far the conclusions adduced for styrene and methyl methacrylate may be extended.

Mr. A. J. Warner (*Ilford*) said: Perrin's very interesting paper omits the commercially important phenomenon of stabilisation of polymerisable hydrocarbons. Since large quantities of styrene are now manufactured and shipped all over the world, it has been necessary to find substances which will prevent the styrene from "thickening up" during transit, whose stabilising effect can be removed by very simple treatment. The most common example is the use of hydroquinone or benzoquinone for this purpose. It has been found that the addition of very small amounts of benzoquinone will enable the styrene to be kept for long periods at room temperature in the presence of air, the stabilising effect being removed by a short heating at an elevated temperature, the subsequent rate of polymerisation being substantially the same as for pure styrene. With substances such as pyrogallol or *m*-dinitrobenzene, however, after an initial induction period, the rate of polymerisation of the styrene is markedly decreased, and these substances must therefore be removed from the styrene before use.

⁶ See discussion, *this volume*, p. 897.

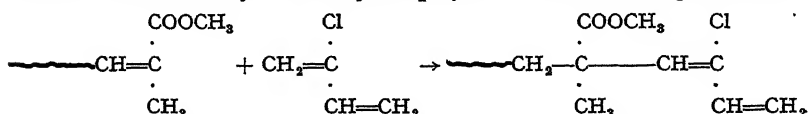
The question of co-polymerisation discussed in the papers of Hill and colleagues, will, I feel, be of great industrial importance in the future development of synthetic plastics. It is interesting to note in this connection that if rubber is dispersed in monomeric styrene and the resultant mass polymerised, a product is obtained which is different from that obtained by milling polystyrene into rubber. It would be of great value if some of the mechanical properties of polystyrene could be modified by co-polymerisation without affecting the extremely good electrical properties of this substance.

Dr. H. W. Melville (*Cambridge*) said: Perrin has raised a number of points of general interest concerning polymerisation reactions. On page 1063 he states that the rate of polymerisation is proportional to $k_1 k_2 / k_3$, where k_1 , k_2 and k_3 are respectively the initiation, propagation and termination velocity coefficients for the several reactions making up the whole process. This expression only holds provided the life of the growing polymer is short compared with the time of reaction and that the active molecules are destroyed at a rate proportional to the first power of their concentration, *e.g.*, by reaction with a suitable inhibitor. There are, however, quite a large number of polymerisations where two active polymers must react before the activity is destroyed. This occurs, for example, in the combination of two free radicals. If the consequences of this type of reaction are worked out, it can easily be shown that the rate is now proportional to $k_2(k_1/k_3)^{1/2}$. The size of the polymer will therefore now depend on the rate of starting, being inversely proportional to the square root of this quantity. The type of termination mechanism has also a bearing in considering the apparent energy of activation for polymerisation. If two active centres disappear together, the contribution made by the starting mechanism to the total energy of activation will be halved on account of the appearance of the square root term. On the other hand, when the rate of termination is proportional to the first power of the growing polymer concentration, the temperature coefficient of the rate of starting will be directly represented in the reaction velocity equation, thus causing the overall energy of activation to be higher than that for mutual destruction of the active centres.

Perrin has also raised the question of the variation of steric factor with molecular size and its possible effect on the velocity of polymeric reactions. In dealing with most reactions, however, it must be remembered that the rate of propagation of the growth of the polymer is really a competitive process; the active polymer either adds on a molecule of monomer, or it interacts with another molecule present in the system, thereby becoming deactivated or destroyed. While the absolute velocity of both processes probably does vary with molecular size, it is the ratio which determines the rate of polymerisation. Moreover, it is highly probable that both these reaction rates vary with molecular size according to the same law and, hence, the rate of polymerisation will not depend on molecular size at all. Some other method must, therefore, be devised to determine whether the steric factor is a function of the size of the molecule. There is, however, one method which provides a direct answer to the question, at any rate for one group of molecules. Under suitable conditions methyl methacrylate, chloroprene and methyl *iso*-propenyl ketone may be induced to grow in the dark from the vapour phase on active polymer produced initially by photochemical activation. Here the rate of growth is determined wholly by the propagation reaction rate. In none of these cases of growth does the rate depend on the length of the molecule over at least a hundred fold range in size.

In the paper by Hill and colleagues it has been shown that butadiene polymerises by means of both 1:2 and 1:4 addition. In another diene, namely chloroprene, there is some experimental proof that the mechanism has a dual character which may be due to the fact that 1:2 and 1:4 addition also occurs in this reaction. When this vapour is illuminated

two polymerisation reactions take place. One is characterised by the fact that the growth continues in the dark, long after the light is cut off; the other stops practically immediately illumination ceases. Now the first kind of growth may be reproduced if chloroprene vapour is allowed access to active methyl methacrylate polymer of the following structure:



and it is supposed that here there is 1 : 2 addition of chloroprene, hence it is thought that the polymer of long life grows by 1 : 2 addition and that of short life by 1 : 4 addition.

Norrish has raised important questions in his communication. He has supposed, in his treatment of the kinetics of polymerisation of styrene and methyl methacrylate, that these molecules interpolymerise with each other. Before this can be done it must first be demonstrated that these molecules are actually incorporated in one and the same polymer molecule. How has this evidence been obtained?

(*Communicated*): A criticism of the interpretation of the mechanism of the polymerisation of methyl methacrylate is as follows: In the liquid phase catalysed polymerisation it has been assumed that the lifetime of the active polymer is comparable with the time of reaction, and that therefore the rate of polymerisation is governed by the rate of the propagation reaction alone. Now it has been shown⁷ that methyl methacrylate can polymerise by two different mechanisms, in one of which the lifetime of the active polymer is long and the other in which it is short compared with the time of reaction. To each of these modes of polymerisation there applies an appropriate kinetic analysis. Hence before that analysis can be applied the lifetime of the active polymer must be known. The nonstationary treatment may be applicable, but also it may equally well be inapplicable; the measurement of the lifetime will at once settle what method must be employed, and thus provide unquestionable proof of the mechanism of the reaction.

Dr. G. Gee (*Cambridge*) said: Hill's proposed mechanism for the emulsion polymerisation of butadiene and its co-polymerisation with methyl methacrylate assumes the reaction to take place at the surface of the emulsion particles. Now it is clear that, in general, emulsion polymerisation may take place in the disperse phase, in aqueous solution, or at the interface between them. The three possibilities may be distinguished by comparing the rate of emulsion polymerisation with the rates in the pure liquid and in a saturated aqueous solution. Some rather crude experiments along these lines support Hill's suggestion for the actual cases he considers, although Fikentscher has previously stated that emulsion polymerisation proceeds in the aqueous phase. It would be of interest to know whether definite evidence of the seat of reaction has been put forward in any other case.

(*Communicated*): In Norrish's written contribution (above) he has represented the number of centres n as an arbitrary function of the catalyst concentration c . It is difficult to imagine any mechanism which does not make n equal or directly proportional to c if we have to assume that the initiation is fast, and in the full account of this work which has now appeared⁸ n is taken to be proportional to c . In this paper Norrish has claimed that for small amounts of catalyst the rate of polymerisation of methyl methacrylate is nearly directly proportional to the concentration of catalyst. Measurements made from the graph representing these data show that the rate is accurately proportional to the square root of the catalyst concentration throughout the whole range examined. From the

⁷ Melville, *Proc. Roy. Soc., A.*, 1937, **163**, 511.

⁸ Norrish and Brookman, *ibid.*, 1939, **171**, 147.

constants of proportionality one can further calculate the energies of activation for polymerisation catalysed by benzoyl peroxide and methyl methacrylate ozonide to be 14.5 and 21.5 kcal./mole resp. Now, according to Norrish's theory these energies should be equal since both should measure the energy of propagation.

It seems to me that Norrish's data can be much more simply explained on the usual view that the initiation is the high energy stage. The fact that the rate is proportional to \sqrt{c} then means that the chain termination process involves two active centres. I do not think one can predict the effect of composition on the rate of co-polymerisation: the variation would only be linear on the very simplest possible assumptions. The variation observed is of a very simple type and it is not surprising that an equation containing four arbitrary constants should represent it quantitatively. The molecular weight increase during the reaction is claimed as strong evidence for Norrish's theory. In fact the curves of Fig. 2 do not fit the equation given (which requires $M \rightarrow 0$ for $\alpha \rightarrow 0$), and since the maximum increase found is by a factor of 2 or 3 only, it remains true that the molecular complexity of the polymers formed at the start of a reaction is of the same order as that of the final product. Two possible explanations of the observed increase may be suggested:

(1) The kinetic evidence indicates that termination occurs by the mutual destruction of two growing chains. This would require the weight average molecular weight to fall 50 per cent. during the reaction provided that the ratio of the velocity coefficients of propagation and termination remained constant. We know, however, that the medium is becoming increasingly viscous, which implies that the long polymer chains are relatively fixed in position while the monomer molecules can still diffuse freely among them. We should consequently expect the efficiency of the termination process to fall and the molecular weight of the product to rise. An upper limit is fixed to this rise by the chain length given by a transfer mechanism in which a growing polymer passes on its reactivity to a new monomer. The ratio of propagation to transfer would not be affected by viscosity and hence the molecular weight becomes constant when this process assumes control, a stage which will be reached earlier when the catalyst concentration (and therefore the number of chains) is small.

(2) In an earlier paper⁹ it has been shown that the benzoyl peroxide catalysed polymerisation of vinyl acetate fails to go to completion at high temperatures or when the catalyst concentration is small because the catalyst is lost by thermal decomposition. Now if the chain length is controlled by a mutual termination process it will be proportional to $1/\sqrt{c}$ and will therefore rise as c falls. It seems to me that this is the probable explanation of the data for methyl methacrylate at 130° C. with 0.005 mols. per cent. BzO_2 (Fig. 2), in which case the reaction would be completed only slowly if at all.

Dr. F. C. Frank (Cambridge) said: There is one point mentioned both by Perrin and Melville which I think should be disposed of: that is the supposition that the steric factor should cause a continual decrease in the reactivity of a growing polymeric chain, not merely for the first few members, but indefinitely. I have never heard of any experimental evidence for this; it is always mentioned for theoretical reasons, and has cropped up on various occasions since I first heard it at the Society's discussion on Polymerisation and Condensation Reactions.¹⁰ *I can see no reason for it whatever.* The collision diameter of the reactive centre is the same whatever the length of chain attached. The point has been stated in the language of the "transition state": but the degrees of freedom of the remoter parts of the chain enter in exactly the same way into the partition functions of initial, transition, and final states, and cancel out

⁹ Cuthbertson, Gee and Rideal, *Proc. Roy. Soc.*, 1939, 170, 300.

¹⁰ *Trans. Faraday Soc.*, 1936, 32, 178.

completely. Naturally there must be a slowing up when polymerisation has progressed so far that the active centre is no longer entirely in an environment of monomer but is partly surrounded by polymer. But that does not imply that it has lost its appetite, merely that it has more difficulty in finding anything to feed on.

Dr. H. W. Melville (*Cambridge*) said: It might be made quite clear that the experimental evidence presented on page 1063 showed that there is no variation in steric factor with molecular size for long molecules. It is therefore quite unnecessary to invoke any theoretical arguments, the validity of which is sometimes open to objection, to discuss the point at all or to dismiss it as trivial matter.

Prof. R. G. W. Norrish (*Cambridge*), in reply, said: In answer to Melville, full evidence of the true co-polymerisation of vinyl compounds is provided by the experiments of Staudinger on the co-polymerisation of styrene¹¹ and divinyl benzene, and by the experiments of Norrish and Brookman on the co-polymerisation of styrene or methyl methacrylate with a wide range of divinyl compounds, including divinyl acetylene and hexatriene.¹² In these cases it was found that the divinyl compound incorporates itself in the growing chains of the monovinyl compound to produce cross links and consequent insolubility. At the same time, however, the co-polymer preserves a strong absorbent effect for would-be solvents leading to a high degree of swelling. The reality of the cross-linking and its physical consequences prove that we are dealing with true co-polymerisation.

Gee, in his written communication, has criticised so strongly the views of polymerisation which I have expressed, that his remarks would seem to demand an equally strong reply if they are to be rebutted. I wish to say at once, however, that I think his criticism so far as it applies to our data respecting the molecular weights is justified, and I regret that in this connection I was not myself sufficiently critical of our results. It must be admitted that good evidence that the molecular weight approaches zero as the degree of polymerisation approaches zero is lacking.

My reluctance to accept the view which Gee now advocates was based on the difficulty of reconciling it with our data on co-polymerisation which indicated unmistakably that chain propagation can be a limiting factor in the reaction. This evidence cannot legitimately be rejected or ignored by my critic: of the four "arbitrary" constants mentioned by Gee, one is negligible and two are fixed by the velocities of polymerisation of the pure styrene and methyl methacrylate respectively. Thus in this case the whole range of velocities of co-polymerisation can be predicted from a knowledge of the velocities of the polymerisation of the two pure substances and one other constant. The form of the curve is accurately predicted by our kinetics: moreover, this is true also of other curves of co-polymerisation of methyl methacrylate or styrene on the one hand with divinyl acetylene or hexatriene on the other, the data for which it is hoped soon to publish. In these cases the variation of velocity is enormously greater: for example, the velocity of polymerisation of methyl methacrylate at 90° C. with 0.005 mols. per cent. of benzoyl peroxide is reduced approximately twenty-fold and ten-fold by the addition of only 1.0 mol. per cent. of hexatriene and divinyl acetylene respectively. Yet co-polymerisation of the different monomeric substances occurs in the same chain, as I have shown above in my answer to Melville.

These facts must be explained by any theory of the process; they presented a difficulty to me in understanding how at one and the same time, chain initiation and chain propagation could be limiting factors.

Gee has pointed out in support of his view, that the velocity of polymerisation of methyl methacrylate can be represented as proportional

¹¹ Norrish and Brookman, *Proc. Roy. Soc., A*, 1937, 163, 205.

¹² Staudinger, *Trans. Faraday Soc.*, 1936, 32, 323.

to the square root of the concentration of the catalyst. Though this fact could be otherwise explained, I acknowledge that the conclusion that the growing chains end by self-neutralisation is the most probable, and it is because I now find that this view can be reconciled with our data of co-polymerisation that I accept it and admit it to give a better explanation of the facts than that which I have advocated heretofore. It must be conceded here by Gee that both chain starting and chain propagation can according to circumstances assume the role of limiting factor controlling the velocity. This arises in the following way: if reaction centres are started at a rate proportional to the concentration of the catalyst (coefficient k) and removed by recombination (coefficient k') their concentration n at any moment is given by

$$n = \sqrt{\frac{k}{k'}} c \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is the concentration of catalyst.

On the simplest view this number n will be dependent only on the catalyst and temperature, and n will therefore be constant under our conditions of co-polymerisation, and independent of the nature of the polymerising medium: thus the condition for our kinetic treatment of co-polymerisation is achieved and by proceeding as described in my contribution, and also in our paper we may deduce as before the rate of co-polymerisation as dependent on four constants of chain propagation in accord with the equation

$$\frac{d\phi}{dt} = \frac{n \left[100k_1 + 2s(k_1' - k_1) + \frac{s^2}{100} \left(\frac{k_1'k_2'}{k_2} - 2k_1' + k_1 \right) \right]}{1 + \frac{s}{100} \left(\frac{k_1'}{k_2} - 1 \right)} \quad . \quad (2)$$

where s is the molecular percentage of styrene in the binary mixture of styrene and methyl methacrylate. On the other hand, if the polymerising medium be kept constant and either temperature or concentration of catalyst be varied, the rate of polymerisation is fixed by the magnitude of n as defined above by equation (1).

This result is inherent in the treatment given by Perrin in his paper. I think that the application of my own kinetic treatment of co-polymerisation to the theory of polymerisation advocated by Gee gives a reasonable explanation of all the known facts. My own expressed view about the growth of molecular weight with time is best forgotten.

Mr. M. W. Perrin (*London*), in reply, said that the mechanism of polymerisation suggested by Norrish referred only to special cases in which it was assumed that there was a constant supply of active centres, so that the polymerisation rate was independent of the velocity of the initiation reaction. In general, the velocity constants of the three reactions corresponding to initiation, growth and termination of the polymer chains are all involved in the expression for the measured velocity of polymerisation. The exact form of this expression will depend on the detailed mechanism of the various reactions, as has been pointed out by Melville on page 1084.

The phenomenon of stabilisation, referred to by Warner, is usually brought about by adding to the monomer a reducing agent which, by reacting with oxygen or peroxides, prevents the catalytic effect of these compounds on polymerisation.

Dr. R. Hill (*Manchester*), in reply, said: Melville has made some observations, which have a limited experimental backing to the effect that chloroprene may undergo 1:2 or 1:4 addition according to circumstances. Evidence by Klebansky and Wassiljewa on the products arising from the ozonolysis of various polychloroprenes, and also X-ray evidence prove that the favoured mechanism is a 1:4 addition. The fact that 1:2 addition may under circumstances occur, is, however, not to be excluded. This eventuality would presumably be governed by the polymerisation

environment which influences the initiation, propagation, and chain ending mechanisms, and so, in turn, the mode of addition. In fact, this falls into line with the conclusion of one of our papers that environment, which in turn is responsible for polymerisation mechanism, is capable of determining whether or no co-polymerisation can be realised.

With regard to Gee's remark, definite evidence that co-polymerisation occurs at the interface and not in the disperse phase or in aqueous solution as supposed by Fikentscher has not yet been obtained. All the evidence we have is circumstantial, but this seems to be sufficiently strong to accept the view which we have in our papers.

Prof. F. O. Rice (*Washington*), in reply (*communicated*) (see pages 870-874): Work in my laboratory has indicated that under certain conditions nitric oxide may stop chains completely, whereas under other conditions it is an inefficient inhibitor. In acetaldehyde and ethers at 300° C., it can completely stop chains but at 500° C. it reduces the chain-length only to about half. Chains of known length were induced by mixing the substrate with very small measured quantities of oxygen; the oxygen induced decomposition could be inhibited by addition of ethyl nitrite which yields nitric oxide; however, complete inhibition could only be obtained at temperatures far below the decomposition temperature of the substrate.¹³

¹³ See Rice and Polly, *J. Chem. Physics*, 1938, 6, 273.

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THE CREAMING OF RUBBER LATEX.

By C. BONDY.

Received 12th September, 1938.

When rubber latex, the milky sap of *Hevea Brasiliensis*, is mixed with small amounts of certain hydrophilic colloids the normally very stable dispersion, on standing, rapidly separates into two distinct layers. The upper layer (cream) contains most of the dispersed rubber hydrocarbon. The major part of the so called serum constituents, *e.g.*, proteins, sugars and electrolytes, is found in the lower layer (skim) which is practically free from suspended matter. The greatly increased rate of separation is due to a loose reversible agglomeration of the rubber particles under the influence of the creaming agent.¹ The concentration of latex by creaming was first suggested by Traube in 1924.² Subsequently creaming processes have found wide application in the rubber industries for the manufacture of latex concentrates. Gums, pectins, gelatin and similar substances are among the hydrophilic colloids that give the best creaming results. The agglomerating action of these materials is not confined to latex alone; the separation of milk, mineral suspensions and other dispersions, is also enhanced by such colloids, one of the most interesting phenomena being the agglutination of red blood cells.³

The mechanism of the aggregation of particles suspended in an aqueous medium is probably similar for all systems which are stabilised by protective agents. The sensitization of distinctly lyophobic suspensions by traces of lyophilic colloids is believed to be due to somewhat different causes. It will, therefore, not be discussed in this paper.

The creaming of latex has been the subject of numerous investigations, and great progress has been made during the last few years in the elucidation of many important points. The actual mechanism of the creaming process appears, however, to be still a matter of considerable controversy. This is borne out by the fact that, only quite recently, two groups of authors put forward two theories which are not readily reconciled with each other.^{4, 5} A further contribution to this interesting problem therefore seems justifiable.

Experimental.

(A) The Adsorption of the Creaming Agent.

A number of theories on creaming involve the assumption that appreciable amounts of the hydrophilic colloid must be adsorbed at the water-rubber interface in order that an agglomeration of the hydrocarbon

¹ H. C. Baker, *Trans. Inst. Rubber Ind.*, 1937, 13, 70.

² I. Traube, Brit. Pat. No. 226440; *Gummi Ztg.*, 1925, 39, 434, 1647.

³ Cf. B. R. Monaghan and H. L. White, *J. Gen. Physiol.*, 1935, 19, 715.

⁴ C. F. Vester, *Proc. Rubber Technology Conference*, London, 1938, p. 126.

⁵ D. F. Twiss and A. S. Carpenter, *ibid.*, II, 81.

particles can take place.⁶ In some cases such an adsorption has actually been observed.^{5, 7} Experiments carried out with sodium alginate as creaming agent led the writer to believe, however, that adsorption was not an essential factor in the creaming process and could even be disadvantageous. These experiments will now be described.

The latex used throughout this investigation was preserved *Hevea* latex. It had a dry rubber content (D.R.C.) of 38.57 % by weight. The aqueous phase contained 1.0 % ammonia, *i.e.*, 0.595 mols. per litre. Experiments were begun about four months after tapping. The creaming agent was a high grade of sodium alginate;⁸ this forms very viscous aqueous solutions, the viscosity depending on the degree of depolymerisation it has undergone during the preparation process. The main sources of alginates are sea weeds. A 0.5 % solution of the product used (in distilled water) had a viscosity of approximately 50 centipoises at 20° C. (extrapolated to zero rate of shear). The determination of the viscosity of alginate solutions affords an easy and accurate means of ascertaining their colloid content. By measuring the viscosity of the skim of creamed latex it is, therefore, possible to find out whether adsorption of the creaming agent has taken place. This method was used by Bächle⁷ and Twiss and Carpenter.⁵ In a series of experiments conducted in very much the same way the writer, in contrast to the authors just mentioned, did not find that creaming was always accompanied by the adsorption of the creaming agent.

The creaming experiments were carried out in stoppered glass tubes, 2.5 cm. wide and 25 cm. long, fitted with narrower outlet tubes at the bottom. The latter could be closed with a piece of rubber tubing and a pinch cock. When creaming was completed the skim was drawn off and its viscosity determined by means of an Ostwald capillary viscometer. Fig. 1 illustrates the results obtained with latex which had been diluted to 30 % D.R.C. In the diagram viscosity is plotted against alginate concentration. Curve 1 refers to latex serum which was prepared by filtration through ceramic filters⁹ and mixed with known amounts of the colloid. The small circles represent results obtained with the skim from creamed latex. The alginate content of the skim was calculated from the amount of colloid originally added to the latex before creaming, *i.e.*, on the assumption that no adsorption had taken place. That this assumption is justified is borne out by the fact that no reduction of the viscosity is found: all the values represented by the small circles coincide with curve 1. If the colloid concentration in the skim had been diminished by adsorption the points would have been situated below the curve. For reasons of comparison the concentration-viscosity curve of alginate solutions in distilled water is also included in the diagram (curve 2). It is seen that the presence of the serum constituents (notably ammonia) is responsible for a considerable decrease in viscosity.

Adsorption may also be measured in a somewhat different way. The amount of adsorbent may be varied and the initial concentration of the substance whose adsorption is studied may be kept constant. According to Freundlich's adsorption isotherm, which is frequently written in the following form,¹⁰

$$\frac{x}{m} = ac^{1/n}$$

the amount of substance adsorbed, x , increases with m , the amount of adsorbent and, therefore, when starting with equal initial concentrations

⁶ P. Stamberger, *The Colloid Chemistry of Rubber*, London, 1929, p. 30; R. J. Noble, *Latex in Industry*, New York, 1936, p. 56.

⁷ O. Bächle, *Kautschuk*, 1936, 12, 232.

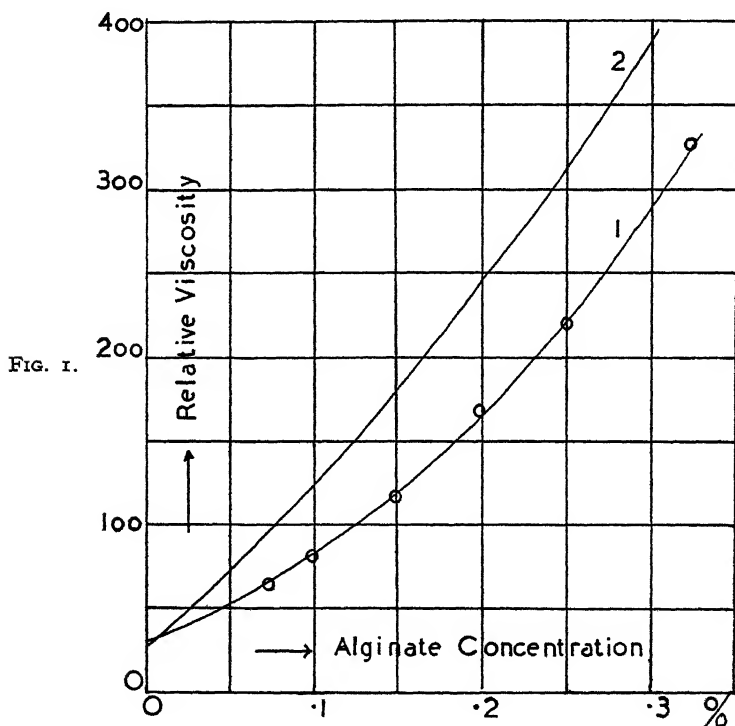
⁸ "Manucol V", a commercial product, manufactured by Messrs. Albright and Wilson, Ltd.

⁹ In the way described by C. Bondy and H. Freundlich, *C.r. Lab. Carlsberg, Sér. chim.*, 1937, 22, 89; *Rubber Age*, N.Y. 1938, 42, 377.

¹⁰ Cf. H. Freundlich, *Kapillarchemie*, Leipzig, 1930, Vol. 1, p. 251.

the equilibrium concentration, c , decreases with increasing amounts of adsorbent, provided that positive adsorption takes place (a and n are constants).

When latex with dry rubber contents varying from 30 to 1.5 % was creamed with 0.15 % sodium alginate (calculated on the aqueous phase) no difference in the viscosity of the resulting skims was found. All the values agreed well with each other and with the control solutions of the indicated initial alginate concentration (0.15 %). The solutions were, of course, so made up as to be equivalent with regard to serum constituents (ammonia, etc.). The fact that here again no appreciable adsorption manifests itself confirms the assumption that adsorption is not an essential factor in creaming.



There is a second and to some extent independent way to show that strong adsorption of creaming agents of the alginate type is not very likely to occur in latex. Latex is a very complex disperse system containing a number of substances which have distinct capillary action at a liquid-liquid interface. These substances will tend to be adsorbed in preference to sodium alginate, which lowers the interfacial tension but very slightly. If adsorption of the creaming agent were a necessary condition for effective creaming it would be very difficult to understand why the addition of capillary active substances such as soaps, far from being detrimental, greatly assist the creaming of fresh latex.¹¹

To investigate this question quantitatively, interfacial tension measurements were carried out, using the drop number method. This method was chosen because of its simplicity, the writer being at the same time fully

¹¹ Naugatuck Chemical Co., B.P. No. 413185.

aware of its short comings.¹² The results cannot claim to be very accurate, but they give a clear-cut answer to the problem under discussion. A stalagmometer with a ground and polished jet and a capacity of 5 ml. was used. The interfacial tension of the aqueous solutions was measured against toluene, the time of outflow of the total volume being 40 minutes. The results are recorded in Table I, from which it can be seen that sodium alginate is far less capillary active than soaps or the substances contained in latex serum. Methyl cellulose, on the other hand (a product with 35.5 % methoxyl was used), shows a substantial lowering of the interfacial tension. This may explain some of the peculiarities exhibited by this substance when used as a creaming agent.⁵ The fact, for instance, that latex cannot be creamed repeatedly by methyl cellulose may be accounted for by the adsorption of the creaming agent, which, by forming a protective film around the rubber globules renders them less susceptible to creaming. The creaming power of methyl cellulose can only be restored by the addition of surface active material which displaces it from the interface.

TABLE I.

Aqueous Medium.	Drop Number.	Approximate Interfacial Tension.	Lowering.
Distilled water	19	35 dynes	—
1 per cent. Sodium alginate solution	21	32 "	3 dynes.
Latex serum	50	13 "	22 "
M/50 Sodium oleate solution	143	5 "	30 "
1 per cent. Methyl cellulose solution	69	10 "	25 "

(B) Precipitation of Emulsifying Agents by Hydrophilic Colloids.

When the creaming of latex was studied, the investigation was extended also to less complex systems, such as toluene emulsions. Thus, emulsions of toluene in water were prepared with sodium oleate, ammonium oleate, gliadin, glutenin, casein, hæmoglobin, gelatin, egg lecithin, sodium cetyl-sulphonate and "Emulfor O" as emulsifying agents. Emulsification was effected by means of ultrasonic waves, as described earlier.¹³ A large increase in the creaming rate of the fairly stable emulsions was found when sodium alginate (0.15 %) was added. The formation of large clusters could be observed under the microscope. The gelatin stabilised emulsions alone showed no sign of induced creaming, but rapid creaming could be brought about by the addition of capillary active materials such as soaps. The following may be the explanation of this effect: the strongly hydrophilic gelatin-coated surface of the emulsion droplets resists the action of creaming agents, but when it is transformed into a soap-coated surface, on which alginates exert a strong influence, aggregation and subsequent creaming ensue.

The concentration of the emulsifying agents, which in these experiments was varied from 0.1 to 1.0 %, appears to be of minor importance for the efficiency of the creaming itself. The cream can be completely redispersed on shaking, which indicates that no coalescence of the droplets takes place.

Hydrophilic colloids, which, as we have seen, need not be adsorbed at the interface, cause cluster formation in well-stabilised emulsions. When attempting to explain this effect one is led to surmise some sort of interaction between the stabiliser and the creaming agent. The occurrence of

¹² Cf. W. Clayton, *Theory of Emulsions and Emulsification*, London, 1923, p. 101 *seq.*

¹³ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, 31, 835.

such an interaction can actually be demonstrated experimentally: sodium alginate will precipitate a number of emulsifying agents from their solutions. The emulsifying agents investigated were of a colloidal or hemicolloidal nature. The effect illustrated in Table II was also found with Caragheen moss, pectin and gum tragacanth.

TABLE II.

"Emulsifying Agent."	Aqueous Medium.	Alginate Conc.	Form of Precipitate.	Time of Formation.
		Per Cent.		
Ammonium oleate (0.6 per cent.)	Dist. water	0.2	Turbid layer on top of clear liquid	24 hours.
Glutenin (1 per cent.)	N/10 NH ₃	0.2	Flocculent sediment	6 hours.
Gliadin (2 per cent.)	N/10 NH ₃	0.4	Emulsion	2-6 hours.
Egg lecithin (0.5 per cent.)	Dist. water	0.2	Fine emulsion	Immediately.
Latex serum	M/50 Borate buffer (pH 9.5)	0.3	Brownish sediment	12 hours.

In control experiments where equivalent amounts of NaCl were added to the solutions instead of the alginate no appreciable change was found. The separation, therefore, must be due to the colloidal anion rather than to the diffusible cation.

The stability of micellar and molecular colloids is usually attributed to two factors: surface potential and solvation.¹⁴ Judging from electrophoretic experiments to be described in the following paragraph it does not seem that hydrophilic colloids reduce the surface charge of stabilised particles to any great extent. It must be assumed, therefore, that the hydrophilic colloid brings about some change in the state of hydration of the stabilising agent. This point will be discussed in more detail later.

(C) Electrophoretic Measurements.

A micro-cataphoresis method was chosen for these experiments. An all-glass cell, consisting of a glass tube with a ground and polished centre part and glass stop cocks at both ends, was used. The cross-section of the tube was a flat ellipse (long axis 4.3 mm., short axis (depth of the cell) 1.5 mm.). The electrodes were coiled platinised platinum wires. Readings were taken at 1/5 of the depth of the cell. Since there is no theory available, as yet, regarding cataphoresis in cells with elliptical cross-section it is not possible to state the exact depth at which the endosmotic flow would be zero. At the indicated depth (1/5) the observed migration velocities appear slightly to exceed the true cataphoretic mobilities, as was found when the cell was tested with substances of which the electrophoretic behaviour is known, *e.g.*, crystallised egg albumin.¹⁵

Latex cannot, as a rule, be used in micro-cataphoretic experiments unless its rubber content is below 0.5 %. For the type of cell used in this investigation further dilution was necessary, usually to about 0.05 %. The cataphoretic mobilities were determined in buffer solutions of 0.01 ionic strength. The hydrogen ion concentration was measured by means of a Morton glass electrode in conjunction with the potentiometer set manufactured by the Cambridge Instrument Co. Ltd. for this purpose.

¹⁴ Cf. H. R. Kruyt, *Colloids*, 2nd edition, London, 1930, p. 192.

¹⁵ T. Svedberg and A. Tiselius, *J. Amer. Chem. Soc.*, 1926, 48, 2272. H. A. Abramson, *ibid.*, 1928, 50, 390.

The results are recorded in Fig. 2. Curve 1 shows the mobility curve of the latex diluted with its own (dialysed) serum. The serum was prepared by filtration through ceramic filters. Curve 2 refers to latex cream obtained by treatment with 0.2 % sodium alginate. The skim, which was practically free from rubber, was dialysed and used for diluting the cream. Curve 3 represents the mobility curve of latex, diluted with distilled water to 0.05 % D.R.C. Curve 4 refers to latex cream diluted with distilled water to 0.05 % D.R.C.

It is seen that the mobility of latex particles is not reduced by the addition of sodium alginate. On the acid side of pH 6 it is even increased, this being probably due to the fixation of alginate ions at the positive

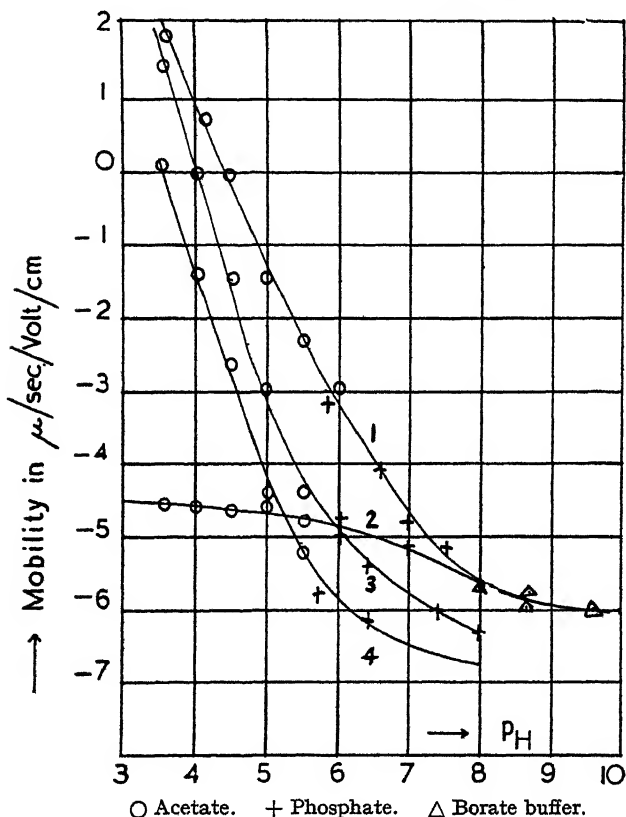


FIG. 2.

NH_3^+ -centres of the zwitterionic protein molecules. On the alkaline side, where all the amino groups may be assumed to be undissociated, no alginate is adsorbed and the mobility curves approach one another very closely. It will be remembered that creaming is, as a rule, carried out in a strongly alkaline medium (pH 9-10). When latex is diluted with distilled water the protein at the rubber surface becomes partly desorbed. This desorption is still more pronounced with creamed latex, as can be seen from curves 3 and 4.

(C) Creaming Rate and Cream Concentration.

The creaming rate and the rubber content of the cream are of paramount importance for the rubber technologist. While the rubber content is,

as a rule, fairly easy to control, the rate of separation depends on more accidental factors, the most important of which seems to be the agitation of the creaming mixture prior to the actual separation. The influence of this factor could in our experiments be eliminated to some extent by violently shaking the tubes with the creaming mixtures for about 60 seconds.

In Fig. 3 creaming curves are recorded which show the influence of alginate concentration on the creaming rate and rubber content of the cream. The creaming mixtures contained 30.8 %. The ammonia content of the aqueous phase was 0.7 %. Creaming was carried out in stoppered measuring cylinders. The skim contained very little or no rubber, except where the alginate concentration was below 0.08 %. The fact that the concentration of the creaming agent largely determines the cream concentrations reached after a given time, already emphasised by various authors,^{5, 16} was confirmed.

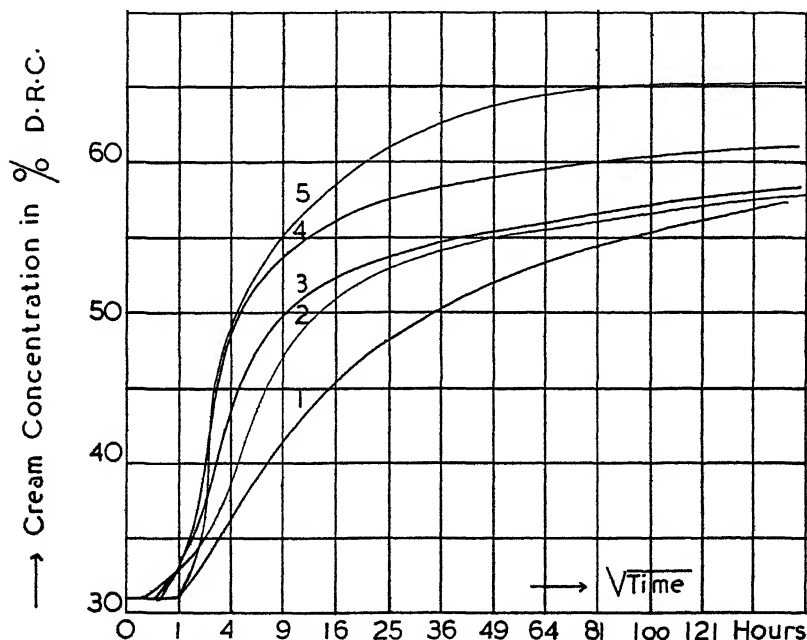


FIG. 3.—Sodium alginate content of aqueous phase: curve 1, 0.303 %; curve 2, 0.242 %; curve 3, 0.181 %; curve 4, 0.121 %; curve 5, 0.061 %.

It is sometimes desired to cream latex which had been diluted, *e.g.*, for the removal of excess serum constituents. When the creaming of diluted latex was studied the somewhat surprising observation was made that the rubber content of the cream ultimately obtained was strongly dependent upon the initial rubber content of the original dispersions. This is illustrated by Fig. 4 in which the creaming curves of diluted latex are recorded. The creaming mixtures contained 0.15 % sodium alginate (calculated on the aqueous phase). The diluent used was 1 % solution of ammonia in distilled water.

This series of experiments was carried out with constant volumes of creaming mixture (25 ml.), the amount of rubber being varied. Similar results are obtained when the amount of rubber is kept constant and the total volumes are varied.

Fig. 5 shows how the rubber content of the cream increases with increasing initial rubber content of the mixtures. Curves 1, 2 and 3 refer

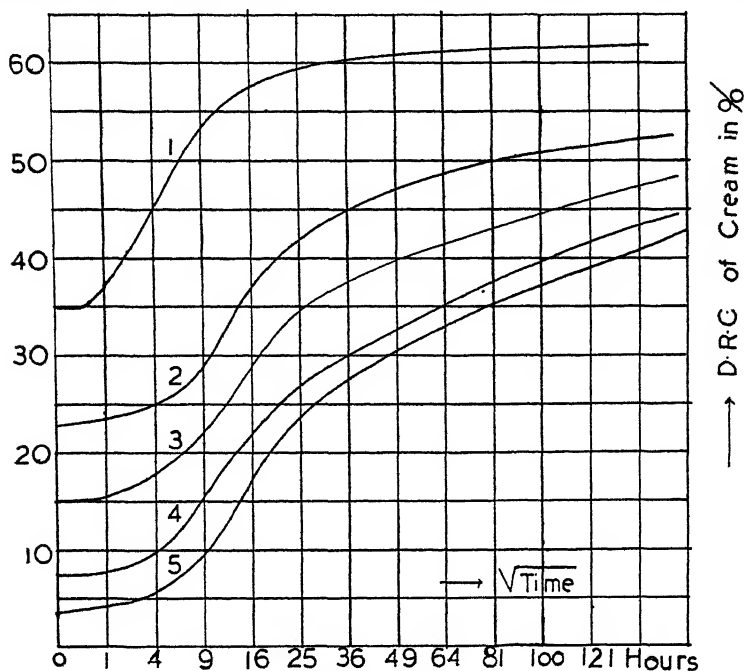


FIG. 4.—Initial rubber contents: curve 1, 35 %; curve 2, 23 %; curve 3, 15 %; curve 4, 7.5 %; curve 5, 3.8 %.

to creaming periods of 24, 50 and 100 hours respectively. The creaming mixtures with rubber contents higher than 35 % were made up from "T-Revertex" a commercial latex concentrate prepared by evaporation,

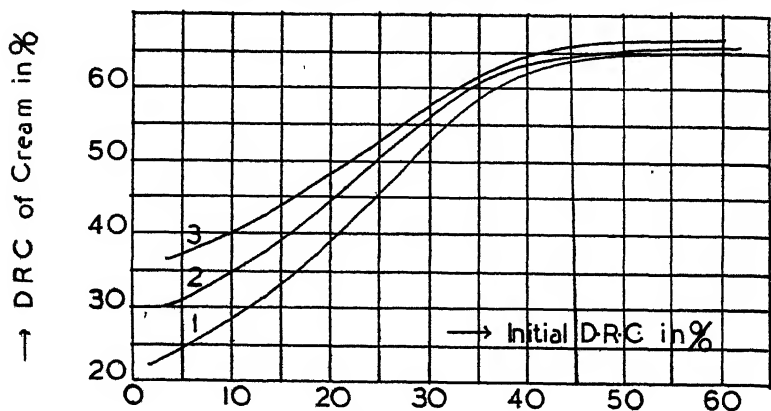


FIG. 5.

which has a D.R.C. of about 60 %, contains no foreign substances save ammonia; and is, therefore, well comparable with normal preserved latex.

The dilution of the serum in no way accounts for the fact that creams with a high rubber content are not obtained from diluted latex. This is borne out by the following experiment. The cream and skim of latex which had been treated with sodium alginate (0.15 %) were mixed in varying proportions. Complete and uniform re-dispersion was achieved by shaking whereby the agglomerates are broken up. Recreaming was then allowed to proceed in the usual way. Table III shows how here again the cream concentration depends on the initial rubber content of the creaming mixture, other factors being equal.

This effect is not found with non-aggregating dispersions, where the packing of the sediment or cream is independent of the initial concentration of the disperse phase. It seems to be a peculiar property of agglomerating suspensions and emulsions.

Experiments with coagulating aqueous suspensions of quartz (in electrolyte solutions) and carbon black showed the same phenomenon, although in a less striking manner. This phenomenon is believed to be common to all disperse systems which have a tendency to form agglomerates.

The structure of the primary agglomerates formed during the first stage of creaming determines the degree of packing in the cream ultimately obtained. The concentration of the dispersion at the start of aggregation appears to determine this structure, which undergoes only a very slow change when the concentration increases during the creaming process itself. It would seem plausible that aggregates formed in concentrated suspensions are more closely packed than those formed in dilute systems where the average distance between the particles is far greater. Fig. 6 suggests the dense structure of an aggregate formed in concentrated suspensions

TABLE III.

Initial D.R.C.	D.R.C. of Cream After 70 Hours.
Per Cent.	Per Cent.
37	57
18.5	38
9.3	35
4.6	33
3.1	31

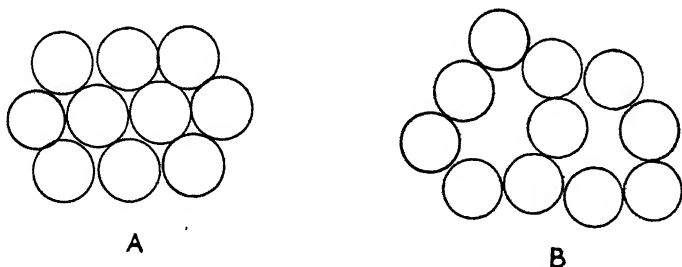


FIG. 6.

(A) as compared with the loose cluster formed in a more dilute suspension (B).

When the cream from dilute latex is separated from the skim and violently agitated so as to break up the primary aggregates, recreaming sets in, yielding a more concentrated cream and fresh clear skim. Thus the rearrangement of the agglomerates at a higher rubber concentration leads to a closer packing. As an example the following experiment may be mentioned. Latex diluted to 7.7 % D.R.C. was creamed with 0.15 % sodium alginate. The cream had a D.R.C. of 45 % after 10 days. Shaking by hand for 60 seconds brought about immediate recreaming and after 24 hours a cream with 59 % D.R.C. was obtained. Instead of shaking by hand any other suitable form of agitation (*e.g.*, stirring) may be employed. Recreaming may be conveniently induced under the action of ultrasonic waves, a smooth and uniform product, free from gas bubbles, being obtained.

Mechanical agitation is not only effective in breaking up large agglomerates, it also favours the aggregation of small particles.¹⁷⁻¹⁹ It, therefore, increases the creaming rate and reduces the induction period during which no visible separation takes place. It furthermore has a definite influence on the cream volume. Fig. 7 shows quantitatively the effect of mechanical agitation. Curve 1 is the creaming curve of a sample which was shaken by hand for 60 seconds immediately after the addition of the creaming agent, curve 2 that of a sample which was left at rest. Both samples were made up from the same creaming mixture: latex with 36 % D.R.C. and 0.1 % sodium alginate. Although creaming curves are not invariably reproducible Fig. 7 is typical.

The creaming of ammoniated latex is but little affected by the presence of electrolytes such as the alkali halides. The alkali chlorides had no marked influence up to concentrations of 600 millimols per litre. Dialysed latex on the other hand is irreversibly flocculated by NaCl or KCl in concentrations higher than 150 millimolar. At lower concentrations the electrolyte has a very unfavourable effect on the creaming process and prevents the formation of a concentrated cream. This effect is due to the

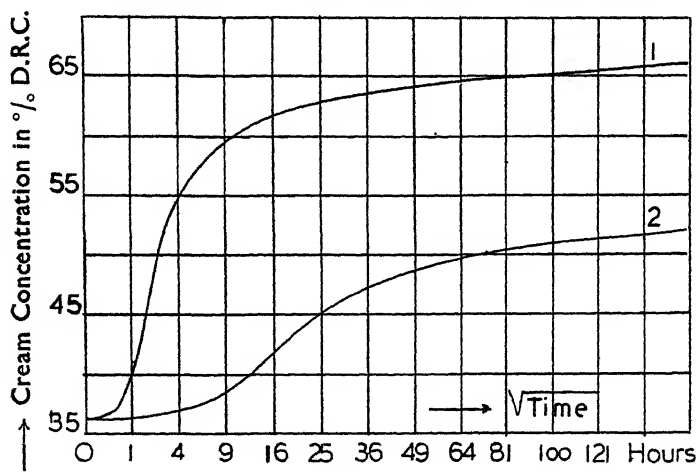


FIG. 7.

destabilisation of the protein coated rubber particles which, in neutral unbuffered solutions, are very sensitive to the presence of electrolytes. The alkali halides influence the cream concentration according to the lyotropic series: $K^+ > Na^+ > Li^+$; $Cl^- > Br^- > I^- > CNS^-$. Calcium sulphate in a concentration of 3-4 millimols per litre strongly increases the viscosity of a creaming mixture containing 0.2 per cent. sodium alginate. This is due to the formation of calcium alginate. The effect on the creaming process is not very marked.

Microscopic Observations.

The agglomeration of rubber particles under the influence of creaming agents can be followed microscopically. For convenient observation a drop of latex is mixed with the practically clear skim obtained when latex is creamed with 0.1-0.3 % sodium alginate. It has sometimes been stated that the Brownian movement of the individual particles is stopped in the

¹⁷ H. H. Paine, *Koll. Beihefte*, 1912, 4, 24.

¹⁸ M. v. Smoluchowski, *Z. physik. Chem.*, 1917, 92, 155.

¹⁹ H. Freundlich and A. Basu, *ibid.*, 1925, 115, 203. J. MacGavack, B.P. 417162; U.S.P. No. 1989241.

presence of creaming agents. This is incorrect ; it is only reduced according to the viscosity of the solutions. Particles in 0.1 % alginate solutions can be seen to move freely though slowly about, in the same way as they do in glycerin solutions of the same viscosity.

The motion is only stopped when larger aggregates are formed. It is remarkable that the viscosity of colloid solutions influences the Brownian movement of small particles without, nevertheless, affecting their cataphoretic mobility. One may conclude from this that at the extremely high rates of shear due to the migration in an electric field the apparent viscosity is reduced to the viscosity of the aqueous dispersion medium.

A close examination of the agglomerates formed reveals a strong tendency to form chain-like aggregates in preference to compact clusters. This is an effect frequently observed with charged particles. It has also been found with latex coagulated with insufficient acid. The pseudo-agglutination (rouleaux formation) of red blood cells seems to be a very similar phenomenon. Usher²⁰ believes that the network structure of thixotropic gels is built up from such aggregates. Latex cream is thixotropic.⁵

The fact that the rubber particles tend to arrange themselves in special patterns suggests that in creaming one is dealing with a process of "slow coagulation" ²¹ where preferably those collisions leading to linear aggregation result in permanent cohesion. This will be mainly true for dilute suspensions ; in concentrated dispersions the particles are so closely packed as nearly to touch each other and the probability of forming compact clusters is far greater.

Discussion.

The foregoing experiments suggest the following mechanism of creaming. The rubber particles owe their stability to the charge and hydration of an adsorbed protein layer. The hydrophilic creaming agent leaves the charge unaffected but owing to its high water-binding capacity it effects a partial dehydration of the adsorbed stabiliser. The result of this is the destabilisation and aggregation of the rubber particles. Strongly hydrophilic stabilising agents will be less affected by the creaming agent. The only particles which will be agglomerated by hydrophilic colloids are those which are coated with substances susceptible to dehydration. Surface active compounds of a polar-nonpolar nature like soaps and lipins are particularly liable to undergo dehydration. It is, therefore, readily understood why the addition of such materials causes a sensitization of particles which carry an adsorption layer of gelatin, methyl cellulose and the like. The surface active substances displace the adsorbed strongly hydrophilic colloid from the interface.

It has been stated in the literature that latex cannot be creamed repeatedly. It may be presumed that such observations were made when capillary active creaming agents were used. After the removal of the serum constituents the rubber particles would be covered by an adsorbed film of the creaming agent which prevents their aggregation. With sodium alginate latex could be creamed six times and more without difficulty.

The mutual dehydration of colloids is a phenomenon which has been known for some time. It has attracted special attention during recent

²⁰ F. L. Usher, *Proc. Roy. Soc., A*, 1929, **125**, 143.

²¹ M. v. Smoluchowski, *loc. cit.*,¹⁸ see also H. Freundlich, *Kapillarchemie*, Leipzig, 1932, Vol. 2, p. 147.

years and is known as coacervation.²² Coacervation is, as a rule, confined to colloids with opposite electric charges, but there are also a few instances known of equally charged colloids showing this phenomenon, *e.g.*, starch and gelatin. Bungenberg de Jong, to whom most of the research in this field is due, has given a very suggestive picture of coacervation. He only takes into account single micelles of hydrophilic colloids, but it seems permissible to extend his views to an entire adsorbed layer. In analogy to Bungenberg de Jong's conception of coacervation the "macro-coacervation" of stabilised particles may be depicted as shown in Fig. 8.

A shows the particle in its original stable form with a thick "diffuse" hydration layer; B represents the partly dehydrated particle with a thin but more "concrete" water envelope; C is an aggregate of dehydrated particles.

Creaming, like coacervation, is a reversible process. When the original conditions are re-established, *e.g.*, by dilution or removal of the creaming agent complete dispersion can be restored. Such reversible phenomena are conveniently discussed in terms of potential curves.²³

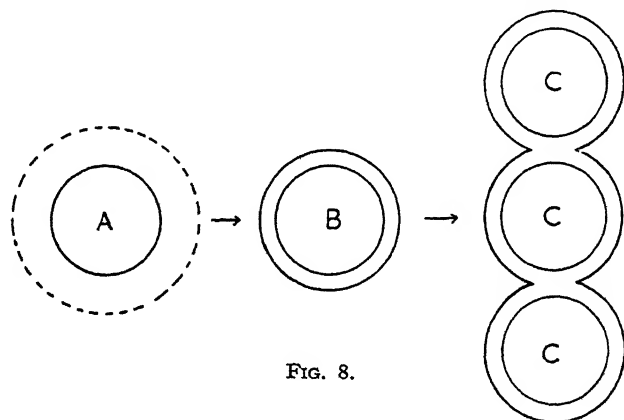


FIG. 8.

The potential energy of two particles with respect to each other is determined by their mutual attraction and repulsion. As a first approximation the repulsion of lyophilic particles can be ascribed to their charge and their solvation, whereas the attraction is due to molecular (London—van der Waals) forces, dipole forces, etc. It is obvious that in stable systems the repulsion forces must be predominant. Since we are dealing with forces of fairly short range there will be no appreciable interaction when the particles are far enough apart. The potential energy will, therefore, be zero at comparatively short distances. Let us assume the repulsion force to be composed of two components, one large and of rather short range representing the elastic forces of the solvation layer, the other smaller but of a somewhat longer range representing the repulsion due to the electric charge. A set of potential curves is drawn in Fig. 9, A. Curve 1 shows the repulsion due to the electric charge, curve 2 that

²² H. G. Bungenberg de Jong and H. R. Kruyt, *Koll. Z.*, 1930, **50**, 39. Cf. also H. G. Bungenberg de Jong, *La Coacervation*, etc., *Actualités Scientifiques et Industrielles*, Paris, 1936.

²³ Cf. H. Freundlich, *Thixotropy*, *Actualités Scientifiques et Industrielles*, Paris, 1935, p. 19; H. C. Hamaker, *Rec. trav. chim.* 1936, **55**, 1015; 1937, **56**, 1, 727.

from the hydration layer and curve 3 the attraction forces. The total potential curve P results from the summation of the three components. Fig. 9, A, depicts a stable system: the total potential energy rises continuously as the particles approach one another. If now we assume a

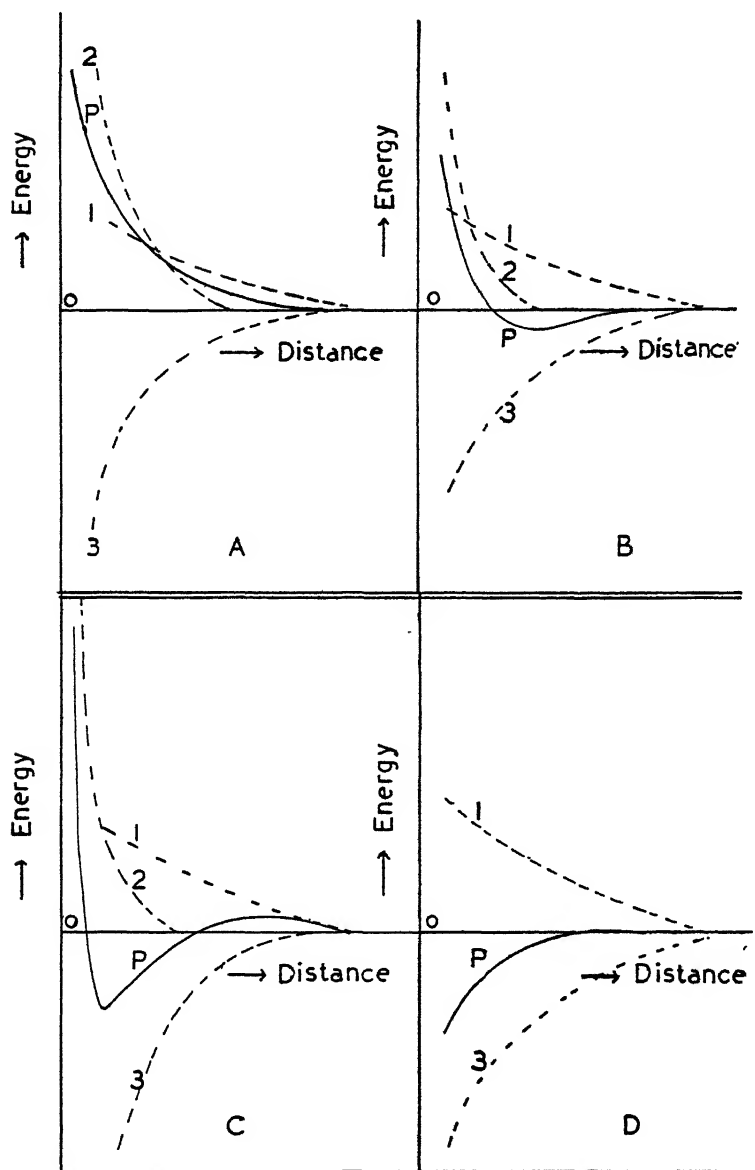


Fig. 9.

dehydration to take place we arrive at a potential curve with a minimum as shown in Fig. 9, B. Here curve 2 has been shifted to the left in accordance with the assumption that the thickness of the solvation layer is reduced. As a result we find that, over a certain range, the attraction

forces prevail: two colliding particles will approach each other till their mutual distance corresponds to the position of the minimum in the potential curve. They will then stick together. The energy required to separate them again is given by the distance of this minimum from the zero line. In the case of creamed latex the minimum must be rather flat since the agglomerated particles can be separated by mere shaking. An alternative possibility for a potential curve with a minimum is given in Fig. 9C. Here a repulsion has to be overcome before two particles can unite. This would mean an activation energy of agglomeration. If dehydration is carried too far, *viz.*, by the addition of large amounts of alcohol, complete coagulation results, because of the predominance of attraction over the whole range of distances (Fig. 9D).

It is apparent from the above consideration that equilibrium in creaming is only reached when all particles are separated from one another by distances corresponding to the position of the minimum in the potential curve. These distances are probably very short and highly concentrated creams should therefore, be expected. It is somewhat difficult to visualise, for such a heterodisperse system as latex, what concentration would correspond to the state of closest packing, but it may be mentioned that the highest concentrations actually observed in creamed latex, *i.e.*, about 67 % by weight or 74 % by volume agree very well with the maximum value as calculated for a system with spherical particles of equal size (74.04 % by volume). In practice it is sometimes impossible to concentrate latex to that extent by creaming. There are factors which disfavour a state of close packing, foremost among which is the strong adhesion of the particles. The experiments of v. Buzagh,²⁴ who made an extensive study of the correlation between sedimentation volume and adhesion, proved that it is only particles with a fair degree of independence of one another which are able to form closely packed sediments. The explanation given by Ehrenberg²⁵ and extended by v. Buzagh, is that particles which show a strong tendency to adhere to one another stick together at random, enclosing large amounts of fluid. They cannot glide over one another when striving to reach positions corresponding to a closer packing and higher degree of order.

Applying this experience, from which hardly any exception is known, to the creaming of latex we can explain some of the peculiarities encountered. It has been stated that the cream volumes increase (cream concentrations decrease) with increasing amounts of creaming agent employed; to account for this we need only assume that the dehydrating action of the hydrophilic colloid is greater in concentrated than in dilute solutions of the creaming agent. From Fig. 9, B it is seen that the minimum in curve P becomes more and more pronounced the more curve 2 (the "hydration curve") is shifted to the left-hand side. This means that it becomes more and more difficult for the aggregated particles to separate and thereby take up more favourable positions. It is not surprising that creaming mixtures, which leave part of the rubber behind in the skim, yield the most concentrated cream. Here the aggregation is only very loose, agglomeration being followed by partial deflocculation until some sort of steady state is reached where there is a constant proportion of agglomerated and free particles. Such a system can reach the equilibrium condition of a closely packed cream in a comparatively

²⁴ A. v. Buzagh, *Kolloidchem. Beih.*, 1930, **32**, 114.

²⁵ P. Ehrenberg, *Bodenkolloide*, Dresden, 1918, p. 83.

short time and shows no "after-creaming". Latex concentrates obtained by creaming with high proportions of creaming agent are not in equilibrium even after many days, as can be seen from the slope of the creaming curves in Fig. 3. Here the high viscosity is probably also an important factor preventing the particles to rearrange their reciprocal positions.

The importance of mechanical agitation for the achievement of good creaming results has been emphasised. Although no attempt has been made as yet to apply Smoluchowski's theory of coagulation to the creaming process—it seems doubtful whether the basic assumptions of his theory hold true in this case—his calculations concerning the effect of stirring on coagulation processes can be used to account qualitatively for the greatly increased creaming rate due to agitation.¹⁸ In a system left at rest only those particles can adhere to each other which, owing to their Brownian movement, enter their mutual spheres of attraction. Now, stirring will bring an additional number of particles into contact. If we assume the sphere of attraction to have a radius equal to the diameter of the particle—this is usually a fair approximation—we can calculate the ratio q of the number of collisions caused by stirring to the number of collisions due to Brownian movement. This ratio is given by the expression

$$q = \frac{4\eta r^3 N \frac{\partial u}{\partial t}}{RT}$$

η being the viscosity, r the particle radius, N Avogadro's number, $\partial u/\partial t$ the rate of shear, R the gas constant, and T the absolute temperature. It is seen that this ratio increases with the third power of the particle size. By stirring at a rate of shear equal to unity the coagulation rate of particles with 1μ diameter is approximately doubled. The formation of larger aggregates increases the influence of stirring very considerably until the clusters reach such dimensions as to be broken up again by the shearing stress. Stirring, therefore, is particularly effective in the early stages of coagulation.²⁶

The mechanism of creaming here suggested is in good harmony with the mechanism proposed by Monaghan and White for the influence of hydrophilic colloids on suspensions of red blood cells.³ These authors, who studied the influence of gelatin on the sedimentation rate of erythrocytes, concluded from electrophoretic experiments that there is no adsorption of the hydrophilic colloid. They ascribed the agglomeration of the red blood corpuscles to a dehydration of the surface. Vester, who also believes dehydration of some serum constituent to be the cause of the creaming of latex, differs from the writer in that he assumes that the formation of a third viscous phase, which envelopes the latex particles and thereby glues them together, is essential for the creaming process.⁴ The fact that latex, which has been deprived of most of its serum constituents by repeated centrifuging or by dilution, can be creamed with the greatest of ease is not in accordance with this view. Such latex contains insufficient amounts of proteins or other substances to give rise to the formation of a new liquid phase on addition of the creaming agent. It should, however, again be emphasised that the presence of an adsorbed layer of a substance, susceptible to the action of creaming agents, seems to be essential for satisfactory creaming and it may at times

²⁶ Cf. H. Freundlich, *Kapillarchemie*, Leipzig, 1932, Vol. 2, p. 157.

be necessary to "sensitise" latex which by purification has become difficult to cream by the addition of soaps or like substances.

Twiss and Carpenter have put forward a theory of creaming fundamentally different from the theories just mentioned.⁵ These authors correlate the creaming action of hydrophilic colloids with the strong structural viscosity of creaming agent solutions. They believe that the forces which are responsible for the high anomalous viscosity are also instrumental in binding together the rubber particles. Thus they suggest "that creaming agent molecules, adsorbed at the surface of the rubber particles, remain capable of taking part in the formation of the loose network system of colloidal particles in the bulk phase." Now this picture is not consistent with one important experimental fact. Creaming agents do not lose, but increase, their aggregating power at higher temperatures where structural viscosity completely disappears (e.g., gelatin above 40° C.).²⁷ Even at temperatures as high as 90° C. where the viscosity of a 0.1 % alginate solution is no higher than that of water at room temperature, there is still no sign of a reduction in creaming power.

The mechanism suggested by Twiss and Carpenter implies the adsorption of the creaming agent, which, as we have seen, although possible,¹⁴ is not essential for the creaming process. An examination of the data given by these authors actually reveals that the adsorption of sodium alginate in their experiments was not very strong. Their results can be represented by an adsorption isotherm of the following form: $x = 2.67c^{1/1.5}$, where x is the amount of alginate adsorbed by 1 g. of rubber (in milligrams) and c the equilibrium concentration (in grams per litre). Isotherms with exponents nearly equal to unity indicate feeble adsorption, as was pointed out by H. Freundlich.²⁸

Summary.

The creaming of latex with sodium alginate as creaming agent has been investigated. Experiments showed that:

1. The creaming agent is not adsorbed at the surface of the rubber particles.
2. The cataphoretic mobility of the particles is not changed in alkaline solutions by the presence of sodium alginate.
3. Sodium alginate precipitates emulsifying agents such as proteins, soaps, lecithin and the like from their (colloidal) solutions.
4. Creaming rates and dry rubber contents of the cream depend on the concentration of the creaming agent.
5. Creaming rates and rubber contents of the cream depend on the initial rubber content of the dispersions. It is believed that sedimentation volumes of aggregating suspensions in general are similarly influenced by the concentration of the disperse phase.

A mechanism of creaming is suggested: creaming agents exert a dehydrating influence on the adsorbed stabilising protein film, thereby causing the rubber particles to adhere to one another. This mechanism and experimental facts are discussed in detail. Other theories on creaming are also discussed.

The author is indebted to Messrs. Revertex, Ltd., London, for a research grant which enabled him to carry out this investigation.

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²⁷ H. G. Bungenberg de Jong, *Rec. trav. chim.*, 1924, **43**, 35.

²⁸ H. Freundlich, *Kapillarchemie*, Leipzig, 1930, Vol. 1, p. 156 seq.

DIFFUSION OF AN AGGREGATING ELECTROLYTE IN THE TRANSITION RANGE FROM SIMPLE TO COLLOIDAL SOLUTION.

BY G. S. HARTLEY.

Received 8th May, 1939.

Although uncharged colloidal particles, or charged particles in an excess of simple electrolyte, diffuse very slowly, it is well known that a pure colloidal electrolyte, in which all the ions of one kind are of colloidal dimensions, diffuses rapidly. This is due, of course, to the colloidal particle having a mobility of the same order as that of a simple ion in the strong electrical potential gradient set up. The diffusion velocity of a pure colloidal electrolyte is thus not at all sensitive to the size of the colloidal ions but very sensitive to the presence of impurity, to a thermodynamic correction term and to an "endosmotic" correction to the mobilities which we know from the work of Onsager and Fuoss¹ to be of peculiar form and considerable magnitude in highly unsymmetrical electrolytes. This latter correction has not been worked out for the type of ionic atmosphere characteristic of a colloidal electrolyte.

For these reasons, the present author, in common with others, has always considered that diffusion measurements on charged colloids must be carried out in excess of simple electrolyte, if quantitative interpretation is to be attempted. Recently, however, Laing-McBain² has published some measurements on the diffusion of higher paraffin α -sulphonic acids in water alone, which reveal a very interesting qualitative feature not previously observed or predicted. She finds that the diffusion velocity, though high in very dilute solutions and, as expected, not very much lower in concentrated solutions, goes through a very low minimum in the region where the acid is passing over from the simple to the colloidal form. She states that this result "cannot be explained on the basis of one kind of colloidal particle," and it is therefore claimed as further proof of McBain's well-known view that "neutral colloid" and "ionic micelle" have a separate existence. The former is supposed to predominate in the transition region, and thus to cause the fall of diffusion coefficient, and the latter in the higher concentrations, where its mobility in the potential gradient accounts for the subsequent rise of diffusion coefficient.

This argument does not take into account one very important point. If only one kind of micelle is present, and that highly charged, it will not contribute as much to the diffusion in the transition region, *where it exists in excess of simple electrolyte*, as it will when it exists in much higher concentration than the simple ions from which it is formed, because *it is acted upon by a smaller potential gradient*. In order to see whether this effect can produce changes of the magnitude found, we may work out the theory in a simple case on classical lines (without introducing any thermodynamic or mobility corrections).

¹ L. Onsager and R. M. Fuoss, *J. Physic. Chem.*, 1932, **36**, 2767.

² M. E. Laing-McBain, *Proc. Roy. Soc., A*, 1939, **170**, 415.

Consider a solution of a single binary electrolyte containing univalent anions in concentration C_1 , z -valent anionic micelles (assumed of one kind only) in equivalent concentration C_z and univalent cations in concentration C_g .

For the rates of transfer, Q , in equivalents per unit time across unit section normal to the gradient, dc/dx , we have, by the Nernst Method,

$$Q_1 = -RT \cdot \frac{dC_1}{dx} \cdot l_1 + FX \cdot C_1 l_1 \quad (1)$$

$$Q_z = -RT \cdot \frac{dC_z}{dx} \cdot \frac{l_z}{z} + FX \cdot C_z l_z \quad (2)$$

$$Q_g = -RT \cdot \frac{dC_g}{dx} \cdot l_g - FX \cdot C_g l_g \quad (3)$$

where X is the potential gradient, F the Faraday equivalent and l 's the velocities in fields producing unit force per equivalent. (The l 's are thus proportional to the ordinary electrical mobilities.)

Substituting for FX from (3) in (1) and (2), adding, and remembering that electrical neutrality requires that $Q_g = Q_1 + Q_z$, we obtain

$$\frac{Q_g}{RT} = -\frac{dC_g}{dx} \cdot l_g + A \cdot C_g \cdot l_g \quad (4)$$

$$\text{where } A = \left(\frac{dC_g}{dx} \cdot l_g - \frac{dC_1}{dx} \cdot l_1 - \frac{dC_z}{dx} \cdot \frac{l_z}{z} \right) / (C_1 l_1 + C_z l_z + C_g l_g)$$

$$\text{whence } \frac{Q_1}{RT} = -\frac{dC_1}{dx} \cdot l_1 - A \cdot C_1 l_1 \quad (5)$$

$$\text{and } \frac{Q_z}{RT} = -\frac{dC_z}{dx} \cdot \frac{l_z}{z} - A \cdot C_z l_z \quad (6)$$

If C is the concentration of the whole electrolyte in equivalents per unit volume calculated without regard to association, the micelle concentration, similarly expressed, is

$$C_m = C - C_1 \quad (7)$$

If now a fraction $(1 - \theta)$ of the charge of each micelle is neutralised by association of gegenions,

$$C_z = \theta \cdot C_m \quad (8)$$

and, by the condition of electrical neutrality,

$$C_g = C - (1 - \theta)C_m \quad (9)$$

The rate of transfer, Q , of the electrolyte as a whole, measured in equivalents without regard to association, will be

$$Q = Q_1 + \frac{1}{\theta} \cdot Q_z \quad (10)$$

$$\text{and also, by definition, } Q = -D \cdot \frac{dC}{dx} \quad (11)$$

Combining (5), (6), (8), (10) and (11) we find

$$\frac{D}{RT} = \frac{dC_1}{dC} \cdot l_1 + \frac{1}{\theta} \cdot \frac{dC_z}{dC} \cdot \frac{l_z}{z} + A(C_1 l_1 + C_m l_z) \cdot \frac{dx}{dC} \quad (12)$$

For the simplest case of $\theta = \text{constant}$, substituting (7), (8) and (9) into (12) we obtain

$$\frac{D}{RT} = l_1 - \frac{dC_m}{dC} \left(l_1 - \frac{l_z}{z} \right) + \frac{l_g - l_1 - \frac{dC_m}{dC} \left(\overline{1 - \theta} \cdot l_g - l_1 + \theta \cdot \frac{l_z}{z} \right)}{l_g + l_1 - \frac{C_m}{C} (\overline{1 - \theta} \cdot l_g + l_1 - \theta \cdot l_z)} \cdot \left[\left(1 - \frac{C_m}{C} \right) l_1 + \frac{C_m}{C} l_z \right] \quad (13)$$

Now l_z/z will be much smaller than l_1 , being approximately inversely proportional to the radius of the micelle. Increase of dC_m/dC will therefore cause a decrease in the second term of (13). In the transition region dC_m/dC must be of course considerably greater than C_m/C , but in higher concentrations both will approach unity. The third term will therefore at first decrease when aggregation begins and subsequently increase. We should thus in general expect a fall of diffusion coefficient followed by a rise again in higher concentrations, which is what is found experimentally.

To obtain a rough estimate of the magnitude of the changes, I have taken the curve for dC_m/dC calculated³ on the mass-action equation for the case of $z = 10$ and $\theta = \frac{1}{2}$ (i.e., m , the number of paraffin-chain ions in the micelle = 20 and n , the number of gegenions = 10) both assumed constant. dC_m/dC in this case rises above unity over a considerable range, reaching a maximum of about 1.12. This means that, during the aggregation of paraffin-chain ions into micelles, the concentration of simple ions decreases absolutely, there being a tendency for the salt to "collapse" completely into the aggregated form. This effect, first predicted by Murray,⁴ has recently received experimental support in measurements of solvent power of paraffin-chain salts.⁵ The rise of dC_m/dC above unity increases the depth of the "valley" in the $D - C$ curve but is by no means the sole cause of it. I have taken l_1 corresponding to 25 in ordinary mobility units, l_g (hydrogen ion) to 350 and l_z to 50. The "Stokes' law mobility" of a micelle containing 20 C_{12} chains, having therefore an overall radius of about 14 Å. and carrying a resultant charge of 10 units would correspond to about 60.

For these figures, calculating D in cm.²/day, we obtain the curve "Th. I" of the figure. Laing-McBain's experimental points in the lower concentrations are given on the figure. They are for the mean diffusion coefficients, \bar{D} , over the concentration range from zero to the concentration specified. To obtain the instantaneous values, D , corresponding to any one concentration, we use the equation

$$D = \bar{D} + C \cdot \frac{d\bar{D}}{dC} \quad . \quad . \quad . \quad . \quad (14)$$

Applied graphically to the broken curve drawn smoothly through the experimental points, we obtain the continuous curve labelled "Exp." The short lines on the right correspond to the asymptotic value for the

³ G. S. Hartley, *Aqueous Solutions of Paraffin-Chain Salts* (Hermann, Paris, 1936), p. 25.

⁴ R. C. Murray, *Trans. Faraday Soc.*, 1934, 31, 206.

⁵ G. S. Hartley, *J. Chem. Soc.*, 1938, 1968.

theoretical curve and to the flat portion of the experimental curve between 0.25 — 1.0 N.

The predicted valley is of comparable magnitude to the experimental. The final value is too high, but no thermodynamic term or mobility correction has been introduced. Curve "Th. II" has been calculated taking $z = 5$ and $\theta = 1/4$ and $l_z = 25$, and assuming dC_m/dc to be the same as for "Th. I." This curve is consistently too low. The concentration scale for the theoretical curves is purely arbitrary and has been selected to give a reasonable fit with the experimental by making $C_m = \frac{1}{2}C$ at a concentration of 0.04 N. The critical concentration, at which dC_m/dc commences to be appreciable and hence at which D commences to fall, becomes then 0.02 N. This is probably too high, but the conductivity data of McBain and Betz ⁶ are not sufficiently numerous in the critical region to enable us to use them for the purpose of fixing the critical concentration.

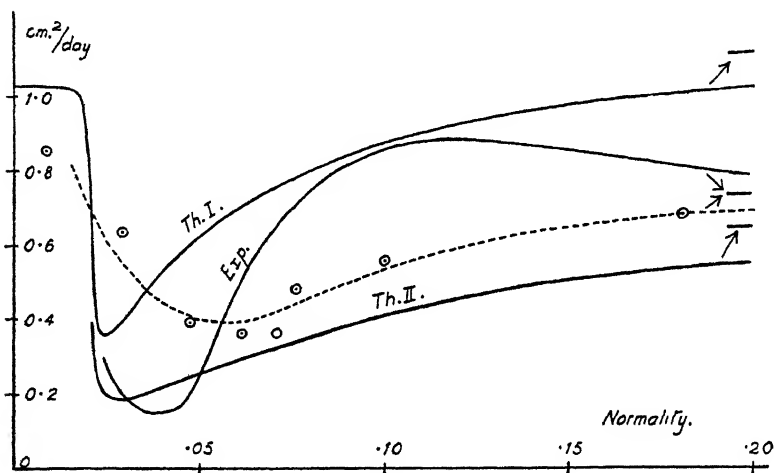


FIG. 1.

In view of the very rough approximations made—constant size of micelle and value of θ , application of mass-action theory to the calculation of dC_m/dc without thermodynamic correction, no thermodynamic and mobility corrections in the diffusion equation—we cannot expect the theoretical curves to be in better agreement with the experimental. All we are concerned to show is that the occurrence of a pronounced minimum in the diffusion-concentration curve is *qualitatively explicable* in terms of the simple theory, put forward by the author and collaborators in recent years in which only one type of micelle is assumed.

Moreover, the experimental data do not appear to justify a more thorough theoretical examination. Though they are of very great interest, the experimental error is unfortunately high and the derived instantaneous diffusion coefficients depend very much on the way in which the smooth curve through the experimental values of \bar{D} is drawn. In the case of the C_{10} acid it is of interest to note that the values of \bar{D} recorded ² for the concentrations 0.0745 and 0.110 N. are 0.704 ± 0.019

⁶ J. W. McBain and M. D. Betz, *J. Amer. Chem. Soc.*, 1935, **57**, 1905.

and 0.292 ± 0.001 respectively. Since the product $D\bar{C}$ for the lower concentration is considerably higher than that for the higher concentration, the values imply a negative average value of D between the two concentrations! Evidently some unforeseen experimental error is present.

Summary.

It is shown how the aggregation of ions in an electrolyte to produce micelles which are mobile in the electric field, may cause a fall of the diffusion coefficient followed by a rise, behaviour the experimental observation of which has recently been reported.

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INFLUENCE OF CERTAIN CARBOHYDRATE SUBSTANCES UPON THE INTERFACIAL TENSION BETWEEN WATER AND CYCLOHEXANE.

BY J. B. MATTHEWS.

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Surface tension and interfacial tension data reveal that when the lowering of the tension is plotted against the concentration of the solution, the type of curve obtained is, broadly speaking, either that mathematically expressed by the well-known empirical equation of Szyszkowski,¹ or a curve, which up to a certain critical concentration appears to follow the Szyszkowski equation, but beyond this critical concentration suddenly flattens off and becomes a straight line. Thus Lottermoser and Winter² have shown that, in the case of the sodium salts of the fatty acids, the lower members of the series give curves of the first type, whereas the higher members give curves of the second type. For intermediate members an intermediate type of curve is obtained. Some investigators have noted a dip, or a minimum, at the critical concentration in curves of the second type.

Harkins, Davies and Clark³ have suggested that the sudden flattening off in curves of the second type is due to saturation of the surface layer, and in view of Rideal and Schofield's⁴ treatment it seems logical to assume that this "saturation" of the surface layer is synonymous with the formation of a condensed film, although Murray⁵ and Powney and Addison⁶ have suggested that the shape of the capillary curves obtained in the case of colloidal electrolytes is a direct reflection of the variation in the concentration of simple long chain ions as the total bulk concentration of electrolyte increases.

¹ B. von Szyszkowski, *Z. physik. Chem.*, 1908, **64**, 385.

² A. Lottermoser and H. Winter, *Koll. Z.*, 1934, **66**, 276.

³ W. D. Harkins, E. C. H. Davies, and G. L. Clark, *J. Amer. Chem. Soc.*, 1917, **39**, 541.

⁴ R. K. Schofield and E. K. Rideal, *Proc. Roy. Soc., A*, 1925, **110**, 167; cf. A. Frumkin, *Z. physik. Chem.*, 1925, **116**, 466.

⁵ R. C. Murray, *Trans. Faraday Soc.*, 1935, **31**, 206.

⁶ J. Powney and C. C. Addison, *ibid.*, 1937, **33**, 1243.

The present investigation has been carried out on aqueous solutions of a group of carbohydrates, ranging from the simple sugars to the complex pectins and gums, the "inert" liquid in contact with the aqueous solutions being pure cyclohexane.

Experimental Method.

The interfacial tension measurements described in this paper were made using a modification of the drop-volume apparatus described by Dredrick and Hanson.⁷ The modification was the substitution of the needle-valve control by a tap control, situated between the dropping tip and the pipette, consisting of a 5 c.c. and a 10 c.c. bulb, which could be used either separately or in conjunction, according to the number of drops required. The whole apparatus was made of Pyrex glass, except for the barrel of the tap, which was made of soda glass. The barrel of the tap had a small V-notch cut into it at either end of the bore of the barrel, so that a fine and accurate control of the rate of flow of liquid through the tap could be obtained. The whole apparatus was mounted rigidly in an air thermostat, by means of which the temperature was maintained at $25^{\circ} \pm 0.1$ C. The tap was operated from outside the thermostat by means of a bell-crank arrangement, the extent to which the tap was open being indicated on a scale by a pointer attached to the tap.

The apparatus was calibrated and the interfacial tension values evaluated by the method already employed by Evans.⁸ The densities of all the solutions were measured, using the Ostwald modification of the Perkin pyknometer,⁹ and were reproducible to the fourth place of decimals.

Since a surface ageing effect occurs for most capillary active substances, it was found necessary to control the life-period of each drop, *i.e.*, the time which each drop spent in growing and finally dropping off. In order to follow the change of interfacial tension with time, measurements were made allowing the drops life-periods of 0.5, 1.0, 2.0, etc. minutes, the method of performing a run being as follows. Each drop was rapidly grown to approximately full-size in about 10 to 15 seconds, when the tap was closed, and then, at the appropriate time, depending on the life-period of the drop, the tap was opened to a position indicated on the scale, corresponding to a rate of flow of one drop in 3 minutes. This procedure was necessary since, as has been shown by Harkins and Brown,¹⁰ the drop-volume is a function of the rate of flow at the moment of detachment of the drop, decreasing with the rate of flow down to a constant value independent of the rate. This constant value for the drop-volume is the value required for purposes of calculation, and with the apparatus used in the present investigation it was obtained for all rates of flow less than that represented by one drop in 2.5 minutes. For life-periods greater than 2.5 minutes "accelerated" runs performed in the way described above, gave identically the same results as were given by runs carried out in the ordinary way, in which the tap is kept open at a position corresponding to a drop rate equal to the life-period of the drop. The accelerated run method effects a very considerable saving in time of experimentation without sacrifice of accuracy.

Reproducibility.

The reproducibility of the measurements varied according to the nature of the aqueous solution which was in contact with the oil phase.

⁷ D. J. Dredrick and M. H. Hanson, *J. Phys. Chem.*, 1933, **37**, 1215.

⁸ A. W. Evans, *Trans. Faraday Soc.*, 1937, **33**, 794.

⁹ W. H. Perkin, *J. Chem. Soc.*, 1884, **45**, 443.

¹⁰ W. D. Harkins and F. E. Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499.

The interfacial tension between water and cyclohexane, which was chosen as the oil phase, was 50.28 ± 0.02 dynes per cm., but the experimental error in the case of the sugar solutions was of the order of ± 0.05 dynes per cm. An error of ± 0.05 dynes per cm. was also obtained in the case of the pectins, gum arabic, and glycogen. For dextrin solutions the reproducibility was remarkably good (within 0.01 dynes) for all concentrations corresponding to the flat portion of the curve (see Fig. 3), but in concentrations corresponding to the downward portion of the curve it was ± 0.05 dynes per cm. Starch and inulin solutions did not give very reproducible results.

The Materials Used.

The liquid used as the oil phase was B.D.H. spectroscopically pure cyclohexane, chosen for its chemical inertness and very high degree of purity.

The water used in making up all solutions was distilled from block tin and then again from quartz, using a quartz spiral reflux and condenser, the steam being superheated before being condensed, and collected in a Jena glass flask.

The dextrose, sucrose, lactose, and starch were of A.R. quality. The dextrin was of Puriss quality, contained 0.6 % ash, and gave a red coloration with iodine. The glycogen and inulin were chemically pure products, and the apple and citrus pectins were B.D.H. products containing 2.0 % and 1.8 % ash respectively. The gum arabic used was a commercial variety of a clear yellow colour. This was hand-picked in order to remove obvious impurities, crushed and ground to pass a 60 mesh sieve. Results were obtained with this crude gum and also with gum which had been purified by precipitation from aqueous solution by the addition of alcohol. Electrodialysis as a means of purification was not resorted to since such treatment yields a product which has markedly different properties from those of the natural gum,^{11, 12, 13} and a preliminary investigation made on the dialysed gum shows that it is structurally different from the original.

All the solutions were made up, allowing for moisture contents, in the cold, except in the case of the starch and inulin solutions. The starch dispersions were made in boiling water, and the inulin solutions were clear solutions obtained by heating the cloudy dispersions made in the cold up to about 80° C. and rapidly cooling. That such treatment of inulin has no appreciable hydrolysis has been shown by Pringsheim, Reilly and Donovan.¹⁴

In connection with the purity of the materials used, Katz and Samwel¹⁵ have made the interesting observation in an investigation of the surface properties of some carbohydrates, that there was remarkable agreement between values obtained for amorphous technical products and purified crystalline products.

Time Effect on Interfacial Tension.

It has already been stated that for solutions and dispersions of capillary active matter a surface "ageing" effect of often considerable magnitude occurs. According to the majority of observers the change in surface or interfacial tension with time extends over several hours and even days,¹⁶ but that this prolonged time effect may be due to chemical

¹¹ G. L. Riddell and C. W. Davies, *J. Physic. Chem.*, 1931, **35**, 2722.

¹² A. G. Norman, *Biochem. J.*, 1929, **23**, 524.

¹³ W. Pauli, E. Russer, G. Schneider, *Biochem. Z.*, 1934, **269**, 158.

¹⁴ H. Pringsheim, J. Reilly and P. P. Donovan, *Ber., B.*, 1929, **62**, 2378.

¹⁵ J. R. Katz and P. J. P. Samwel, *Liebig's Ann. der Chemie*, 1929, **472**, 241.

¹⁶ R. M. Reed and H. V. Tartar (number of references given), *J. Amer. Chem. Soc.*, 1936, **58**, 322.

interaction at the interface is suggested by the fact that it has been shown to be so in the case of the surface-tensions of soap solutions, *cf.* Lottermoser and Baumgürtel.¹⁷ Apart from any ageing effect due to chemical interaction at the interface, it seems quite definite that an ageing effect, extending over periods of the order of one minute, does take place. Although Lottermoser and Baumgürtel¹⁷ were unable to measure the "times of

TABLE I.

Substance.	Equilibration Time, (Minutes).	Coefficient of Diffusion.
Dextrose	Not detectable	0.5 (15° C.)
Sucrose		0.5
Lactose		0.5
Dextrin (a)		0.14
Dextrin (b)	1-2	0.14
Apple pectin	0.5	—
Citrus pectin	5	—
Gum arabic	4	—
Glycogen	1	0.24 (20° C.)
	4	—

equilibration" of the soaps from the formate up to the laurate, yet further on in the series the observed time of equilibration was found to increase with chain length and dilution, and to decrease with increase of temperature. This suggests very strongly that the time effect is due to slow diffusion to the interface, but a second possibility, that it may be due to molecular rearrangement at the interface itself cannot be dismissed.

In the present investigation the change of interfacial tension with time has been observed in a roughly quantitative way by allowing the drops life-periods of 0.5, 1.0, 2.0, 3.0, etc. minutes in different runs. That the tension measured is that of a surface of age equal to the life-period of the drop is indicated by the fact that for life-periods greater than 2.5 minutes (the minimum time for drop formation to give the true drop volume)

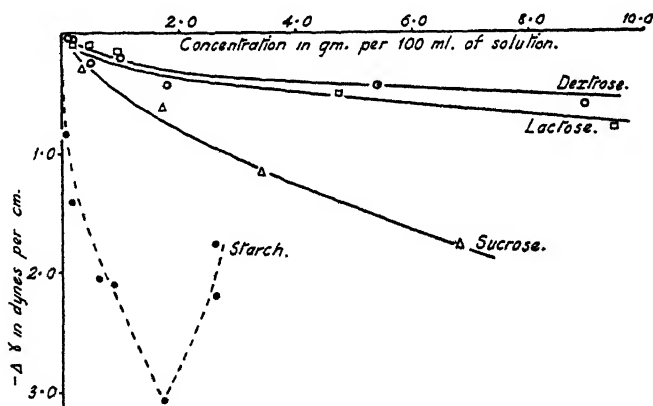


FIG. 1.

the same value for the tension is obtained in accelerated runs as in ordinary runs.

The results obtained for the equilibration times of all the substances used, except starch and inulin, for which it was not possible to obtain values because of the erratic behaviour they exhibit at the interface, are given in Table I. The coefficients of diffusion have been obtained from the International Critical Tables, and refer to 25° C., unless otherwise

¹⁷ A. Lottermoser and B. Baumgürtel, *Trans. Faraday Soc.*, 1935, 31, 200.

stated. Within the limits of observation the equilibration time was found to be independent of concentration, except in the case of dextrin, for which substance the equilibration time was 1 to 2 minutes in the concentrations corresponding to the downward portion of the curve, and only 0.5 minutes in concentrations corresponding to the flat portion of the curve. In these two regions of concentration the time of equilibration was apparently independent of concentration. The fact that the coefficients of diffusion do not support the view that the equilibration times are the times required for diffusion of solute molecules to the interface, suggests that the times recorded are the times required for molecular orientation at the interface. As orientation times, however, they are very much greater than one would expect.

The interfacial tensions plotted in Figs. 1, 2, and 3 are equilibrium values, except those for starch and inulin. For starch and inulin it is impossible to obtain true equilibrium values.

Discussion.

The results obtained for the sugars are plotted in Fig. 1, in which the abscissæ represent the concentrations in gms. per 100 ml. of solution, and the ordinates ($\Delta\gamma$) represent the differences between the interfacial tensions of the solutions and that of pure water. As we would expect, the type of curve obtained is the type associated with a gaseous film at the interface at all concentrations. The dextrose molecule possesses a ring structure, and the sucrose and lactose molecules consist of two rings linked together, and from analogy with the chain compounds studied by Rideal and Schofield,⁴ Adam,¹⁸ Langmuir¹⁹ and others, the lateral adhesion between such molecules will not be sufficient to cause the formation of a condensed film at the interface. It is interesting to note that sucrose occupies an anomalous position with regard to dextrose and lactose. This is probably related to the fact that the sucrose molecule consists of a pyranose ring combined with a furanose ring, whereas lactose consists of two pyranose rings linked together, the molecule of dextrose consisting of one pyranose ring.

On the basis of his theory of surface tension Dole²⁰ obtained the following expression for the energy of adsorption of capillary active molecules at a surface :

$$-W = RT \ln \left[1 + \frac{1}{RTk} \left\{ \frac{d(\gamma_0 - \gamma)}{dc} \right\}_0 \right],$$

where W is the energy of adsorption per gm. molecule, R is the gas constant, T is the absolute temperature, k is the thickness of the adsorption layer divided by 1000, c the molar concentration, γ the surface tension of the solution, and γ_0 the surface tension of the pure solvent. This equation is essentially the same as that deduced by Langmuir.¹⁹ Applying it to the case of the interfacial tensions of the three sugars investigated, and taking 5 Å. as the thickness of the adsorption layer,*

¹⁸ N. K. Adam, *Proc. Roy. Soc., A*, 1921, 99, 336.

¹⁹ Langmuir, *J. Amer. Chem. Soc.*, 1917, 39, 1848.

²⁰ M. Dole, *ibid.*, 1938, 60, 904.

* Katz and Samwel¹⁵ obtained values between 4 and 5.5 Å. for the thickness of surface films of the acetates of various carbohydrates, and from X-ray measurements the thickness of the hexose chain is given as between 4 and 5 Å. E. G. Cox, T. H. Goodwin and A. I. Wagstaff, *J. Chem. Soc.*, 1935, 1496. Schofield and Rideal give 4.66 Å. as the thickness of the sucrose molecule, *Proc. Roy. Soc., A*, 1925, 109, 73.

the values obtained for W , expressed in calories per gm. molecule are : dextrose, -800 ; lactose, -1560 ; sucrose, -1830 , the negative sign indicating positive adsorption. The energy of adsorption of the lactose molecule is rather less than twice that of the dextrose molecule; which is to be expected, since the lactose molecule consists of two pyranose rings. Sucrose, on the other hand, has an energy of adsorption more than twice that of dextrose. If we can assume that the energy of adsorption of the pyranose ring in sucrose is equal to the energy term which characterises it in the lactose molecule, it follows that the furanose ring in sucrose contributes an energy of adsorption equal to -1050 calories per gm. molecule.

According to Haworth, Hirst, and others,^{21, 22, 23} the dextrin unit consists of a practically straight chain of pyranose units, the number of which per chain varies from four (Schardinger's dextrin) up to 17

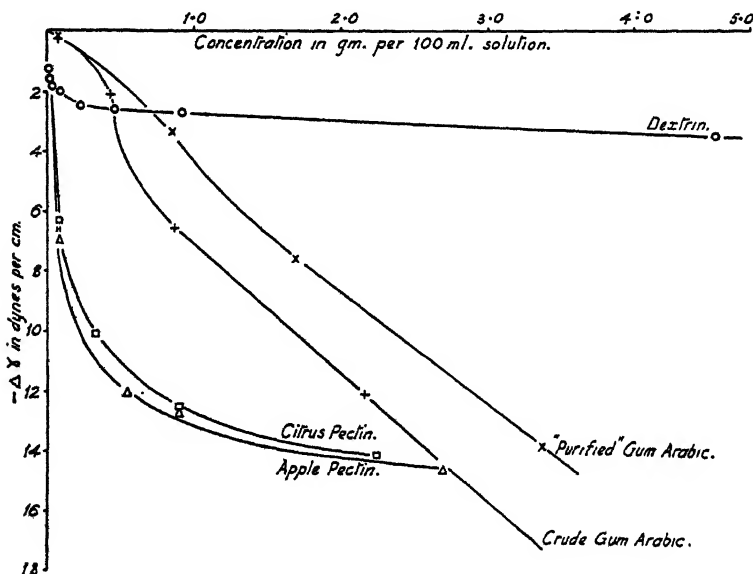


FIG. 2.

(amylopectin). The dextrin used in the present investigation was an erythropectin, giving a red coloration with iodine, and probably had a chain length between 8 and 12 pyranose units.* Such dextrans show no tendency to aggregate,²¹ and so the molecules in solution consist of the fundamental units. A surface film of such molecules, by reason of their long, narrow shape, should be capable of forming a condensed film, and from the capillary curve for dextrin, shown in Fig. 2,

²¹ W. N. Haworth, E. L. Hirst and M. M. T. Plant, *J. Chem. Soc.*, 1935, p. 1214.

²² W. N. Haworth, E. L. Hirst and A. C. Waine, *ibid.*, p. 1299.

²³ K. Freudenberg and R. Jacobi, *Liebigs Ann. der Chemie*, 1935, 518, 102.

* The coloration produced with iodine is a function of the particle size and two dextrans have been isolated, of chain lengths 8 and 12 units, both giving a red coloration with iodine (W. N. Haworth, E. L. Hirst and M. M. T. Plant, *J. Chem. Soc.*, 1935, 1299).

it can be seen that this is what actually does happen. Applying the Dole equation to the region of low concentrations, and assuming the molecule to consist of 6, 8, 10 units, the corresponding energies of adsorption are: -950 , -730 , and -660 calories per unit, respectively. Since the energy of adsorption per unit was -800 calories in dextrose, and -780 calories in lactose, it follows that in all probability the chain length of the dextrin used was eight units.

Gum arabic, Fig. 2, shows no tendency to form a condensed film at the interface, the curve showing no sign of flattening off. According to Butler and Cretcher²⁴ the gum arabic molecule is composed of one molecule of *d*-glucuronic acid, three molecules of *d*-galactose, three molecules of *l*-arabinose and one molecule of *l*-rhamnose. Pauli and Palmrich²⁵ state that gum arabic, purified by electrodecantation and electrodialysis, acts in all concentrations as though built up of the same elementary complex, containing seven monoses. From viscosity measurements Coumou²⁶ has shown that gum arabic does not show any evidence of long chain structure, and this view is supported by the type of curve shown in Fig. 2, which is essentially a gaseous type. It will be noticed that "purification," by precipitation from aqueous solution with alcohol, has raised the curve, which is in agreement with the general lowering effect the presence of free electrolytes has upon the interfacial tensions of solutions of capillary active matter.²⁷ "Purification" lowered the ash content from 2.8 % to 2.6 %, presumably by removing free electrolyte, since it has been shown in a preliminary experiment that hydrolysis causes a fundamental change in the shape of the molecule, the type of curve obtained for arabic acid being a condensed type. Taking Butler and Cretcher's constitution of the gum arabic molecule as being correct, the energy of adsorption per gm. molecule, using the data for the purified gum, and assuming that the thickness of the adsorption layer is 5 Å., is -3700 calories. If we take the energy per pyranose unit as being -730 calories, as for dextrin, then it follows that only five of the seven pyranose units in the gum arabic molecule are adsorbed at the interface. This is what one would expect if the gum arabic molecule is of a spherical shape, for such molecules, when they become adsorbed, will tend to spread out on the surface, but will not be able to spread completely to give all the constituent units the opportunity to become adsorbed at the interface.*

From Fig. 2 it is seen that citrus and apple pectins give almost identical curves, which belong to the intermediate type. There is obviously a tendency to form a condensed film at the interface, but evidently the lateral attraction forces between the molecules are not strong enough to bring this about. According to Schneider and Bock²⁸ pectic substances have an open, long chain structure, which view is supported by X-ray studies²⁹ and by Coumou's viscosity measurements,²⁶ but the interfacial tension data obtained indicates that the

²⁴ C. L. Butler and L. H. Cretcher, *J. Amer. Chem. Soc.*, 1929, **51**, 1519.

²⁵ W. Pauli and L. Palmrich, *Koll. Z.*, 1937, **79**, 63.

²⁶ J. Coumou, *Chemisch. Weekblad*, 1935, **32**, 426.

²⁷ J. Powney and C. C. Addison, *Trans. Faraday Soc.*, 1937, **33**, 1253.

* If only five of the seven constituent units of the gum arabic molecule are adsorbed at the interface, the thickness of the adsorption layer will be 10 Å. and not 5 Å. Using the former figure the energy of adsorption becomes -3500 cal., which still indicates that 5 units are adsorbed.

²⁸ G. G. Schneider and H. Bock, *Ber., B*, 1937, **70**, 1617.

²⁹ See F. A. Henglein and G. Schneider, *ibid.*, 1936, **69**, 309.

ratio of length to thickness of the pectin molecules is not great enough to cause the formation of a condensed film at the interface. This is in agreement with the recent work of Hirst and Jones,³⁰ who ascribe a main chain with branches as the molecular structure of the araban component of apple pectin, since the presence of the side chains will add considerably to the thickness of the molecule.

As is to be expected, the type of capillary curve obtained when the lowering of the interfacial tension is plotted against the concentration depends on the type of surface film existing at the interface, which in turn depends on the shape of the solute molecules constituting this film. This deduction is borne out by a comparison of the results obtained for the three carbohydrates, dextrin, glycogen and inulin, shown in Fig. 3. Because of the long, more or less straight chain form of its molecule, dextrin gives a capillary curve of the condensed type, showing a sudden flattening off when the surface layer becomes sufficiently

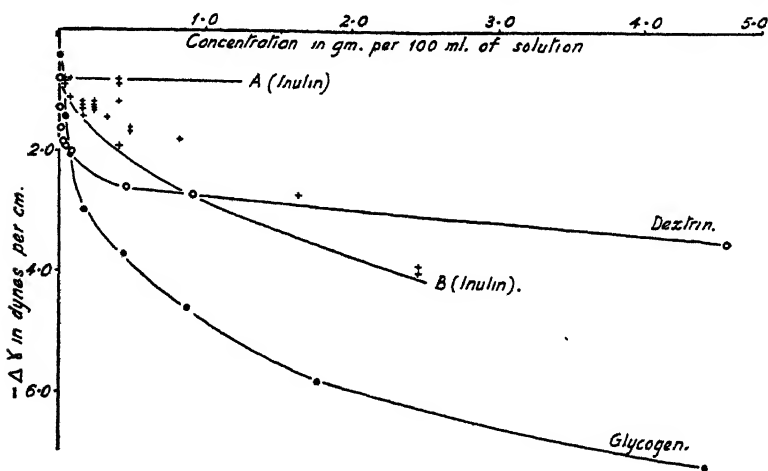


FIG. 3.

concentrated to form a condensed film. The glycogen molecule, on the other hand is spherical,³¹ and hence glycogen is unable to form a condensed film at the interface, even though, according to Haworth, Hirst and Isherwood,³² the glycogen molecule contains at least either 12 or 18 units whereas the dextrin molecule only contains 8 units. The inability of glycogen to form a condensed film is shown by the capillary curve it gives, which is an intermediate, vaporous, if not a truly gaseous type. Taking the thickness of the adsorption layer to be 15 Å,* and assuming the molecule to consist of 12 units the energy of adsorption is -4700 calories per gm. molecule, which corresponds to 6 units being positively adsorbed at the interface. If we take the molecule as 18 units the energy of adhesion is -5000 calories per gm. molecule, which corresponds to 7 units being adsorbed. It is apparent that the ad-

³⁰ E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1939, 454.

³¹ H. Staudinger and E. Husemann, *Liebigs Ann. der Chemie*, 1937, 530, 1.

³² W. N. Haworth, E. L. Hirst and F. A. Isherwood, *J. Chem. Soc.*, 1937, 577.

* Katz and Samwel (*Liebigs Ann. der Chemie*, 1929, 472, 241) obtained values between 14.5 and 15.7 Å. for the thickness of the surface film of glycogen acetate.

sorbed molecule has become somewhat flattened out at the interface, as was the case with gum arabic, and if we consider the adsorbed molecule to consist of three tiers of either 6, 4, 2, or 7, 6, 5 units, we obtain an adsorption film of approximately 15 Å. thickness.

Inulin shows a remarkable behaviour. Even though a life-period of 3 minutes per drop was strictly adhered to in all the inulin interfacial tension determinations, yet widely varying results were obtained, especially in a certain region of concentration. When all the values are plotted they are found to lie between two hypothetical curves, namely A, a condensed type of curve, and B, an expanded type of curve. This suggests that the surface film in the case of inulin solutions is heterogeneous, consisting of both expanded and condensed regions. That inulin should behave in this erratic manner at the interface is probably connected with the irregular "hairpin" structure which has been attributed to the inulin molecule by Haworth, Hirst and Percival.³³

The results obtained for starch, given by the broken line in Fig. 1, cannot be considered to be of much significance from the point of view of interfacial tension. In the low concentration region the lowering effect is not as great as would be expected from a chain length of 24 units,³⁴ in comparison with the lowering effect of dextrin, and for higher concentrations the tension apparently becomes raised. There is little reproducibility, however, in this higher concentration region. In this region, a skin of gelatinous starch was observed to form at the interface. The fact that starch precipitates out at the interface in this manner can be attributed to its molecular structure. According to Hirst, Plant and Wilkinson³⁴ the starch molecules "owing to their particular conformation possess greater facilities for aggregation and interlocking (as compared with cellulose)." We can thus imagine the adsorbed starch molecules becoming interlocked, catching up others from the bulk of the solution, with the result that gelatinous starch precipitates at the interface. The formation of this skin explains the anomalous results obtained, for even in the low concentrations the tensile strength of the skin will become superimposed on the interfacial tension, and so give higher results than would be expected. In the higher concentrations it is essentially the tensile strength of this skin which is being measured, and this increases both with concentration and with age of surface.

Summary.

(1) Interfacial tension measurements have been made on aqueous solutions of various carbohydrate substances against cyclohexane.

(2) In all cases (except those of starch and inulin) equilibrium values are recorded, *i.e.*, the ageing process, which is of the order of minutes, has been completed.

(3) The shape of the capillary curve obtained when the lowering of the interfacial tension is plotted against the concentration is shown to depend on the type of monomolecular surface film existing at the interface, which in turn depends on the shape of the carbohydrate molecules constituting this film. The existence of gaseous, condensed, and heterogeneous adsorption films is indicated. Thus, it is concluded that whilst molecules of dextrose, lactose, sucrose and gum arabic form gaseous films

³³ W. N. Haworth, E. L. Hirst and E. G. V. Percival, *J. Chem. Soc.*, 1932, 2384.

³⁴ E. L. Hirst, M. M. T. Plant and M. D. Wilkinson, *ibid.*, p. 2375.

over the entire range of concentration investigated, dextrin gives a non-condensed film at low concentrations, a condensed film above a critical concentration. Citrus and apple pectins give an intermediate type of film, glycogen a film approximating to a vaporous one. In the case of starch no conclusions could be drawn as to the surface orientation.

(4) On the basis of Dole's theory it is possible to calculate in a number of cases the energy of adsorption which characterises certain ring structures.

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REVIEWS OF BOOKS.

The Theory and Use of the Complex Variable. By S. L. GREEN.
Isaac Pitman & Sons Ltd. London: 1939. Pp. viii and 136 + 8.
Price 10s. 6d.

This book should be invaluable to students of electrical engineering or hydrodynamics. The first four chapters should, however, appeal to a much wider circle. Their usefulness can be gauged by the chapter headings:

1. Complex numbers and their representation.
2. De Moivre's theorem.
3. Infinite series. The exponential, logarithmic, circular and hyperbolic functions.
4. Functions of a complex variable. Conjugate functions. Cauchy's theorem. Contour integrals.

To read this book the preliminary equipment required is only a knowledge of calculus (including partial differentiation) and analytical geometry, that is to say, no more than every physical chemist ought to possess.

E. A. G.

Actualités Scientifiques et Industrielles. (Paris: Hermann and Co., 1937.)

I. Biochimie de la Choline et de ses Dérivés. I. Choline-Neurine.
By ERNEST KAHANE—JEANNE LEVY. (Pp. 61. Price 15 francs.)

A monograph dealing with the chemistry, properties and physiology of choline and neurine. An adequate short account is given.

III. L'Activité électrique de L'Écorce cérébrale. By FRÉDÉRIC BREMER. (Pp. 46. Price 15 francs.)

This review upon the subject mentioned is an account of a conference in April 1937, held under the auspices of the Société Philomathique de Paris. It has been made more complete by the inclusion of important work which has appeared since the conference, and represents an introduction to the subject.

Protective Coatings for Metals. By R. M. BURNS and A. E. SCHUH.
(London: Chapman & Hall, 1939. Pp. 407. Price 32s. 6d.)

This Monograph is a contribution to the series of scientific and technical writings sponsored by the American Chemical Society and the National Research Council whose enterprise reached its culminating point in the Critical Tables of Chemical and Physical Constants. The avowed object of the present publication, that of furnishing a well-digested survey of the progress already made in the subject and of pointing out directions in which investigation needs to be extended, has been well fulfilled. The work shows clear evidence of being up-to-date and of definite industrial value. The various main systems for applying protective coatings which now hold the field may be enumerated in the order of their development as hot-dipping, electro-deposition, metal-spraying or atomising and the use of lacquers, enamels and pigments. One is left in some difficulty in deciding which of these systems can, at the present time, claim to be of the greatest industrial importance. Among outstanding recent developments which are disclosed by this monograph reference may in particular be made to a process recently introduced in this country for electro-galvanising steel wire and strip which pass through the cells at a speed of 200 feet per minute, employ a cathodic current density of 2000 amps., per square foot, and a total current per cell of 40,000 amps. the electrolyte being made direct from zinc ore concentrates and giving a metal of 99.99 per cent. purity.

Other notable advances dealt with are spray processes, oxide coatings by "anodising" and the application of resistant enamels made from more than a thousand varieties of pigments, cellulose lacquers and natural or synthetic resins. An important component of this type of coating which is considered at some length is the accompanying oil solvent, or plasticiser.

Innovations are notified in sherardising by zinc powder, calorising by aluminium powder, chromising, cementation by other metals, "metal-cladding" and cathodic sputtering. Detailed consideration has been given to the physical properties of different coatings, the purposes of their application and their resistance in different environments. Separate chapters are devoted to methods of testing the resistance; the adhesion of coatings; the measurement of permeability; the mechanism of corrosion; the durability and evaluation of paints; and paint plastics.

J. N. P.

The Alloys of Iron and Nickel. Vol. I. Special-Purpose Alloys.
By J. S. MARSH. Alloys of Iron Research, Monograph Series.
(New York and London: McGraw-Hill Publishing Co., 1938. Pp. xii + 593. Price 36s.)

The Iron Alloys Committee of the Engineering Foundation in America is rendering a valuable service in publishing this series of monographs, in which the literature of the subject is very thoroughly surveyed, an attempt to sum up the situation at the end of each chapter being a special feature of the series. Nickel being the metal which has the widest range of application as an alloying element in steels and cast irons, it has been found necessary to divide the account of its alloys with iron into two volumes. The second will deal with the engineering properties, whilst

the present work is devoted to a description of the iron-nickel system and to those alloys which are used for special purposes on account of their exceptional properties. Some of these are highly anomalous. Thus invar and its allies, with a coefficient of expansion which is small and in certain states almost zero, and alloys of extremely high magnetic permeability, such as permalloy, have properties which could not have been predicted from the existing knowledge of binary systems of two closely related metals. Unfortunately, the determination of the equilibrium diagram of the system has proved to be extraordinarily difficult. The atoms of the two metals are very similar to one another, so that diffusion in the solid state is slow, and equilibrium on annealing is only attained very slowly, if at all. Hence there is no general agreement as to the form of the equilibrium diagram. Several important papers on the subject have appeared since the publication of this volume.

In this connection the structure of meteoric irons is of the first importance, and it is to be regretted that the author has made only the barest references to this subject. It must be supposed that these cosmic bodies, consisting essentially of alloys of iron and nickel, must have had ample opportunity for reaching equilibrium in the course of geological ages, and their structure is most clearly developed, and on a very coarse scale, yet the artificially prepared alloys exhibit no such structure. (The alleged reproductions of meteoric structure are quite unconvincing.) Osmond's scheme of a eutectoid system has been abandoned by most metallurgists, and a simple system, affected by a large hysteresis, substituted, although recent work by Bradley suggests that the phase diagram is actually complex. X-ray studies present difficulties on account of the similarity in scattering power of the iron and nickel atoms, but Owen has lately obtained useful results by means of a high-temperature camera. The fact remains that of all the binary diagrams of the important metals this is the system which is known with the least certainty.

The present volume contains a very large body of data concerning the alloys. Some sections, particularly that dealing with the invar group, are behind existing knowledge, and the general impression is that of a rather undigested mass of facts, but it must be admitted that the author has had a very difficult task, and the many references to the bibliography of 619 items in chronological order will prove helpful to the student.

C. H. D.

INTERACTION BETWEEN TWO HYDROPHOBIC COLLOIDAL PARTICLES, USING THE APPROXIMATE DEBYE-HÜCKEL THEORY. I. GENERAL PROPERTIES.

BY S. LEVINE AND G. P. DUBE.

Received 27th March, 1939.

1. Introduction.

In two previous papers,¹ a first and second approximation were obtained for the interaction energy of two metallic colloidal particles, using the approximate Debye-Hückel equation in the theory of electrolytes.* The method adopted to calculate the energy proved to be rather laborious and hence it was found desirable to develop an alternative method,† which permits the determinations of the higher approximations without too much difficulty. In another paper, appearing elsewhere,² we have developed the general formulæ for the interaction energy for any approximation and have also given the results in detail for the first three approximations. In this report we shall examine these results.

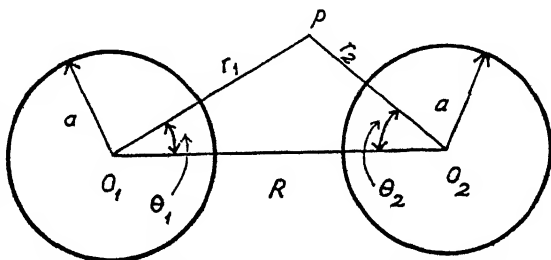


FIG. 1.—Two Colloidal Particles at Distance R .

For the sake of completeness, we shall repeat the problem to be solved. We consider two identical spherical colloidal particles O_1 and O_2 , each of radius a at a distance R apart (Fig. 1), immersed in water,

¹ S. Levine, *Proc. Roy. Soc., A*, 1939, **170**, 145, 165. Also G. P. Dube and S. Levine, *Comptes rendus*, 1939, **208**, 1812 (preliminary note).

* Professor F. London has informed one of us (G.P.D.) that he also obtained an approximate expression for the interaction energy of two colloidal particles which is similar to ours. He worked out these calculations some years ago (1935), also with a view to explain Thixotropy. He got the peculiar result that on the basis of the Debye-Hückel theory, two similarly charged colloidal particles do attract each other at large distances. The expression he obtained is identical with the asymptotic value of our first approximation at large distances (including both the positive and negative terms). His calculations have, so far, not been published due to certain objections raised by H. Kallmann (private communication to Professor London) which we cannot consider to be valid any longer. We are thankful to Professor London for his permission to publish this note.

† Of course, the same formulæ as in the previous work were obtained for the first two approximations.

² S. Levine and G. P. Dube. In the press.

containing an electrolyte. The potential ψ at any point in the water is assumed to satisfy the approximate Debye-Hückel equation,

$$\nabla^2\psi = \kappa^2\psi, \quad (1)$$

where κ is the characteristic quantity in the Debye-Hückel theory being proportional to the square root of the electrolyte concentration. We wish to evaluate the change in energy associated with the charges on the particles and their ionic atmosphere as the two particles approach one another. As already explained,¹ we need to consider,†

$$F_2 = -\frac{D\kappa^2}{8\pi} \int_V \psi^2 dv + \int_{S_1} \sigma \Psi dS_1, \quad (2)$$

where D is the dielectric constant of the electrolytic solution and σ and Ψ are the charge density and potential respectively at any point on either one of the particles, say O_1 . The first integral on the right-hand side of (2) is taken over the volume V of the solution surrounding the two particles and the second integral over the surface S_1 of the particle O_1 . When the two particles are at infinite separation F_2 reduces to $2F_1$, where F_1 is the energy associated with a single particle and has the form¹

$$F_1 = \frac{Q^2}{2Da(1+\tau)} \left\{ 1 - \frac{\tau}{2(1+\tau)} \right\} = \frac{Q^2}{Da} f_0(\tau), \text{ say, } \tau = \kappa a. \quad (3)$$

The change in energy as the two particles approach one another is then given by $F_2 - 2F_1$.

The appropriate solution of (1) is expressed as an infinite series, with terms whose coefficients will depend on the boundary conditions chosen at the surface of the particles. Here, we shall deal with two particular cases, namely insulating and metallic particles.

It has already been mentioned¹ that the first term roughly implies linear superposition of the charge distributions in the double layers of the two particles. In a similar fashion, it is possible to give simple interpretations of the manner in which the higher terms in the series for the electric potential account for the distortion in the ionic atmospheres. The second term corresponds to an induced effective dipole, the third term to an induced quadrupole and so on.

In § 2 the expression for the interaction energy is given; in § 3 the boundary conditions used to determine the coefficients are given and in § 4, we interpret the physical nature of the various terms in the expressions for the electric potential and energy. In § 5, our theory is compared with those of Langmuir³ and Derjaguin⁴ and in § 6, the relation of our results to the Debye-Hückel theory for true electrolytes is discussed.

† The quantity F_2 is the work of charging the two particles and the excess of ions in their diffuse layers under the following conditions: (1) the particles are fixed in position during the process; (2) the temperature is constant; (3) κ is constant, which is legitimate for dilute sols; and (4) the potential, acting on the ions, is the additional potential gained on entering the field of the particles, since this potential only varies with the particle distance. For the linear equation (1), this work is equal to the average energy.

¹ I. Langmuir, *J. Chem. Physics*, 1938, 6, 873.

⁴ B. Derjaguin and M. Kussakov, *Acta Physicochimica*, U.S.S.R., 1939, 10, 25, 153; B. Derjaguin, *ibid.*, 1939, 10, 333.

2. Derivation of Interaction Energy.

In order to find an expression for F_2 , it is first necessary to transform the surface integral in (2) into a more suitable form. For metallic particles Ψ is constant over the surface of each particle, so that

$$\int_{S_1} \sigma \Psi dS_1 = \Psi \int_{S_1} \sigma dS_1 = Q\Psi \approx Q\bar{\Psi}, \quad (4)$$

remembering that the total charge on each particle is,

$$Q = \int_{S_1} \sigma dS_1. \quad (5)$$

In actual practice, we shall deal with an approximate form for the potential which will consequently not be constant over the surface of each particle. It is found convenient to replace Ψ by its average value,

$$\bar{\Psi} = \frac{1}{4\pi a^2} \int_{S_1} \Psi dS_1 = \frac{1}{2} \int_0^\pi \Psi \sin \theta_1 d\theta_1 \quad (6)$$

over the surface of the particle. When dealing with insulating particles, we shall assume a uniform distribution of charge of surface density $\sigma = Q/4\pi a^2$ on each particle.* In this case the surface integral in (2) again becomes $Q\Psi$, just as for metallic particles.

The first three terms in the infinite series representing the solution of (1) read⁵

$$\left. \begin{aligned} \psi_3 = A & \left[\frac{e^{-\kappa r_1}}{r_1} + \frac{e^{-\kappa r_2}}{r_2} \right. \\ & + \lambda_1 \left\{ \cos \theta_1 \left(1 + \frac{1}{\kappa r_1} \right) \frac{e^{-\kappa r_2}}{r_1} + \cos \theta_2 \left(1 + \frac{1}{\kappa r_2} \right) \frac{e^{-\kappa r_1}}{r_2} \right\} \\ & + \frac{\lambda_2}{2} \left\{ (3 \cos^2 \theta_1 - 1) \left(1 + \frac{3}{\kappa r_1} + \frac{3}{(\kappa r_1)^2} \right) \frac{e^{-\kappa r_1}}{r_1} \right. \\ & \left. + (3 \cos^2 \theta_2 - 1) \left(1 + \frac{3}{\kappa r_2} + \frac{3}{(\kappa r_2)^2} \right) \frac{e^{-\kappa r_2}}{r_2} \right\} \left. \right] \\ & = A(\phi_0 + \lambda_1 \phi_1 + \lambda_2 \phi_2), \text{ say,} \end{aligned} \right\} \quad (7)$$

where the coefficients A , λ_1 and λ_2 are determined by applying the boundary conditions. Here r_1 and r_2 are the distances from any point in the solution to the centres of the two particles and θ_1 and θ_2 are the angles shown in Fig. 1. For any approximation we shall always express A in terms of λ_1 and λ_2 by applying Gauss' theorem in electrostatics, namely,

$$-\frac{4\pi Q}{D} = \int_{S_1} \left(\frac{\partial \psi}{\partial r_1} \right)_{r=a} dS_1 \left(= \int_{S_2} \left(\frac{\partial \psi}{\partial r_2} \right)_{r_2=a} dS_2 \right).$$

On putting $dS_1 = a^2 \sin \theta_1 d\theta_1 d\bar{\phi}_1$, where $\bar{\phi}_1$ is the azimuthal angle about the line O_1O_2 , this becomes

$$-\frac{2Q}{Da^2} = \int_0^\pi \left(\frac{\partial \psi}{\partial r_1} \right)_{r_1=a} \sin \theta_1 d\theta_1, \quad (8)$$

yielding

$$A = \frac{Qe^\tau}{D(I + \tau) I - \delta_1(I + \alpha)}, \quad (9)$$

* A discussion of this point is given in paper II.

⁵ Cf. G. Scatchard and J. G. Kirkwood, *Physik. Z.*, 1932, 33, 297; J. G. Kirkwood, *J. Chem. Physics*, 1934, 2, 351.

where

$$\delta_1 = \frac{e^{-\tau(s-2)}}{2s\tau} \left(\frac{\tau-1}{\tau+1} + e^{-2\tau} \right); \quad \alpha = \lambda_1 \left(1 + \frac{1}{s\tau} \right) + \lambda_2 \left(1 + \frac{3}{s\tau} + \frac{3}{(s\tau)^2} \right). \quad (10)$$

Adopting the same notation as in the two previous papers, we have put $s = R/a$ so that $\kappa R = s\tau$.

We shall evaluate, instead of the expression (2),

$$F_2^{(3)} = Q\bar{\Psi}_3 - \frac{D\kappa^2}{8\pi} \int_V \psi_3^2 dv, \quad (11)$$

where $\psi_3 = \Psi_3$ on the surface of each particle. The reason for this approximation has already been previously discussed¹ (see also § 3). Then it can be shown that²

$$F_2^{(3)} - 2F_1 = \frac{Q^2}{Da} f_3(s, \tau) = \frac{Q^2}{Da} \{f_r^{(3)}(s, \tau) + f_a^{(3)}(s, \tau)\}, \quad (12)$$

$$\text{where} \quad f_r^{(3)}(s, \tau) = \frac{(\delta_1 + \delta_2)(1 + \alpha)}{(1 + \tau)\{1 - \delta_1(1 + \alpha)\}}, \quad (13)$$

$$\text{and} \quad f_a^{(3)}(s, \tau) = \frac{\tau}{2(1 + \tau)^2} \times \left[1 - \frac{\delta_{00} + 2\lambda_1\delta_{01} + 2\lambda_2\delta_{02} + \lambda_1^2\delta_{11} + 2\lambda_1\lambda_2\delta_{12} + \lambda_2^2\delta_{22}}{\{1 - \delta_1(1 + \alpha)\}^2} \right], \quad (14)$$

$$\text{with} \quad \delta_2 = \frac{e^{-\tau(s-2)}}{2s\tau} (1 - e^{-2\tau}), \quad (15)$$

$$\delta_{nm} = \frac{\kappa e^{2\tau}}{2\mu} \int_V \phi_n \phi_m dv. \quad (16)$$

The suffixes r and a imply that the two contributions to the energy are of a repulsive and attractive nature respectively. This property has already been previously discussed to some extent.¹

Explicit expressions for δ_{nm} have been obtained and the reader is referred to the mathematical paper² for details. The forms for δ_{00} , δ_{01} , and δ_{11} † have already been obtained¹ by elementary methods of integration.

It is possible to give the general nature of the forms of the quantities δ_{nm} . In the product $\phi_n \phi_m$, according to the expressions given in (7), there will be two types of terms, those involving r_1 and θ_1 (or r_2 and θ_2) only and the cross terms involving r_1 , θ_1 , r_2 and θ_2 . When $n \neq m$, the first type will lead to a contribution, which we shall denote by $\delta_{nm}^{(1)} + \delta_{nm}^{(11)}$, such that,

$$\delta_{nm}^{(1)} = e^{-2s\tau} R_{nm}^{(1)}(s, \tau), \quad \delta_{nm}^{(11)} = R_{nm}^{(11)}(s, \tau) \int_{\tau(s-1)}^{\tau(s+1)} \frac{e^{-2y}}{y} dy,$$

and the cross term will contribute $\delta_{nm}^{(111)} = e^{-s\tau} R_{nm}^{(111)}(s, \tau)$. Here $R_{nm}^{(1)}$, $R_{nm}^{(11)}$, and $R_{nm}^{(111)}$ are rational algebraic functions of their respective arguments. When $n = m$, there is an additional term $\delta_{nn}^{(0)}$ in the first type, which depends only on τ . Since δ_{00} is comparatively simple, we shall give its complete expression as an illustration,†

† In the previous papers we used the notation, $\delta_{00} = 1 + \delta_s$, $\delta_{01} = \delta_4 + \delta_s$, $\delta_{11} = \delta_6 + \delta_7$, $\delta_{00}^{(1)} + \delta_{00}^{(11)} = -\mu_1$, $\delta_{00}^{(111)} = \mu_2$, but the present notation is more appropriate. Also, the explicit forms for δ_1 , δ_2 and δ_{00} are expressed somewhat differently here.

$$\left. \begin{aligned} \delta_{00} &= \delta_{00}^{(0)} + \delta_{00}^{(1)} + \delta_{00}^{(11)} + \delta_{00}^{(111)}, \\ \delta_{00}^{(0)} &= 1, \quad \delta_{00}^{(1)} = -\frac{e^{-2\tau(s-2)}}{8s\tau} \{2\tau s + 1 - 1 + (1 - 2\tau s - 1)e^{-4\tau}\}, \\ \delta_{00}^{(11)} &= \tau e^{2\tau s^2} \frac{1}{2s} \int_{\tau(s-1)}^{\tau(s+1)} \frac{e^{-2y}}{y} dy, \quad \delta_{00}^{(111)} = \frac{e^{-\tau(s-2)}}{s\tau} (1 - e^{-2\tau} + \tau s - 2). \end{aligned} \right\} \quad (17)$$

The energy expressions (12), (13), (14) constitute a third approximation to the true form. A first approximation is obtained by putting $\lambda_1 = \lambda_2 = 0$ and a second by putting $\lambda_2 = 0$. We shall replace $f_3, f_s^{(3)}$ and $f_a^{(3)}$ by $f_1, f_s^{(1)}$, and $f_a^{(1)}$ for the first approximation and by $f_2, f_s^{(2)}$, and $f_a^{(2)}$ respectively for the second approximation.

3. Boundary Conditions to Determine the Coefficients.

For metallic particles the boundary condition to be satisfied is that Ψ be constant over the surface of each particle, the value of Ψ being determined by applying Gauss' theorem (8). When dealing with a finite number of terms (say 3), in the series for the potential, it is impossible to satisfy this condition, which must, therefore, be replaced by some approximate condition leading to reasonable values for the coefficients λ_1 and λ_2 . One method of determining λ_1 and λ_2 is to assume that the potential has the same value at the two end points $\theta_1 = 0, \pi$ and on the great circle $\theta_1 = \pi/2$ on the surface of the particle O_1 (with analogous conditions for the particle O_2). In the earlier work,¹ where we only considered the first two terms in the potential, the two end points were taken to have the same potential. However, we shall suggest two other methods of choosing convenient conditions. All the three methods will be compared in II.

It should be remembered that all the boundary conditions will refer to one particle only, say O_1 . However, since the solution chosen will be symmetrical with respect to O_1 and O_2 it follows that the corresponding conditions at the surface of the second particle will be automatically satisfied.

The simplest choice is to assume that the first moment of Ψ_3 about the plane $\theta = \pi/2$ is zero, *i.e.* $(\mu_1 = \cos \theta_1)$

$$\int_{-1}^{+1} \mu_1 \Psi_3(\mu_1) d\mu_1 = \int_0^\pi \cos \theta_1 \Psi_3(\cos \theta_1) \sin \theta_1 d\theta_1 = 0, \quad (18)$$

and that the corresponding second moment is equal to two-thirds of the average value of $\Psi_3(\mu_1)$,

$$\int_{-1}^{+1} \mu_1^2 \Psi_3(\mu_1) d\mu_1 = \frac{2}{3} \bar{\Psi}_3 \quad (19)$$

These two conditions† would be automatically satisfied if Ψ_3 were constant.

† It should be remarked that the choice of these conditions is not purely arbitrary, but arises from the properties of the Legendre polynomials which appear in the expression for the electric potential. This also refers to insulating particles.

The second and perhaps the most accurate method is to choose λ_1 and λ_2 , so that the mean square deviation of Ψ_3 from its average value over the surface of each particle is a minimum,† *i.e.*

$$G(A(\lambda_1, \lambda_2); \lambda_1, \lambda_2) = \int_0^\pi (\Psi_3 - \bar{\Psi}_3)^2 \sin \theta_1 d\theta_1 = \text{minimum}, \quad (20)$$

subject to the condition (8). This implies that $\partial G/\partial \lambda_1 = 0$ and $\partial G/\partial \lambda_2 = 0$, remembering that $A(\lambda_1, \lambda_2)$ is given by (9) as a function of λ_1 and λ_2 .

When dealing with the first approximation ($\lambda_1 = \lambda_2 = 0$) there is no question of determining λ_1 and λ_2 and the constant A is given by (9) with $\alpha = 0$. For the second approximation ($\lambda_2 = 0$) we need only use the condition (18) to determine λ_1 or alternatively take $\partial G/\partial \lambda_1 = 0$. Here $A(\lambda_1)$ is given by (9) with $\lambda_2 = 0$.

For the insulating particles we need to solve Laplace's equation for the potential χ inside the particles,

$$\nabla^2 \chi = 0 \quad . \quad . \quad . \quad (21)$$

simultaneously with (2). The solution of (21) corresponding to (7) reads,

$$\chi_3^{(1)} = B_0 + B_1 r_1 \cos \theta_1 + \frac{B_2}{2} (3 \cos^2 \theta_1 - 1) r_1^2 \quad . \quad (22a)$$

inside particle O_1 , and

$$\chi_3^{(2)} = B_0 + B_1 r_2 \cos \theta_2 + \frac{B_2}{2} (3 \cos^2 \theta_2 - 1) r_2^2 \quad . \quad (22b)$$

inside particle O_2 .

The boundary conditions to be satisfied are the ordinary ones holding at the boundary between two dielectric media, namely

$$\psi \equiv \Psi = X \equiv \chi \text{ at } r_1 = a, \quad . \quad . \quad . \quad (23)$$

$$\left(\frac{\partial \psi}{\partial \theta_1} \right)_{r_1=a} = \left(\frac{\partial \chi}{\partial \theta_1} \right)_{r_1=a}, \quad . \quad . \quad . \quad (24)$$

$$\sigma = \frac{Q}{4\pi a^2} = -\frac{D}{4\pi} \left(\frac{\partial \psi}{\partial r_1} \right)_{r_1=a} + \frac{D'}{4\pi} \left(\frac{\partial \chi}{\partial r_1} \right)_{r_1=a}, \quad . \quad . \quad (25)$$

where D' is the dielectric constant inside the particles. We have denoted the value of χ at the surface of each particle by X (with $X_3 = \chi_3$). The same boundary conditions hold for O_2 also. On integrating (25) over the surface of O_1 , we readily obtain Gauss' theorem (8).

When using the exact solutions for ψ and χ the condition (24) follows from (23), *i.e.* (23) and (25) are sufficient to determine the coefficients uniquely. However, when dealing with a finite number of terms in the infinite series for ψ and χ , we must again replace (23) and (25) by some approximate conditions. We shall only use the simplest method for determining the coefficients, namely the moment method. There are

† For the sake of further reference, we shall designate the first method of determining the coefficients as the *moment method*, the second as the *least square method*, and the one adopted in the earlier papers¹ as the *point method* (described at the beginning of this section).

five coefficients to compute,** λ_1, λ_2 ; B_0, B_1 and B_2 , remembering that (9) expresses A in terms of λ_1 and λ_2 .

It is of interest to discuss the connection between the energy form (11) and the boundary conditions. The formula (11) is the simplest but not the only one that could be used to find F_2 . An alternative expression for F_2 is (treating the insulating case)

$$F_2 = -\frac{D}{8\pi} \int_V |\text{grad } \psi|^2 dv - \frac{2D'}{8\pi} \int_{v_1} |\text{grad } \chi|^2 dv, \quad (26)$$

which is identical with (2) provided we use the correct forms for ψ and χ , i.e. the infinite series. The second integral on the right-hand side of (26) is taken inside the volume v_1 of particle O_1 . On applying Green's theorem it is readily seen that (26) becomes,

$$F_2 = -\frac{DK^2}{8\pi} \int_V \psi^2 dv - \frac{1}{4\pi} \int_{S_1} \left(D\Psi \frac{\partial \psi}{\partial r_1} - D'X \frac{\partial \chi}{\partial r_1} \right)_{r_1=a} dS_1. \quad (27)$$

substituting (1) and (21). Unless the boundary conditions (23) and (25) are strictly satisfied, the surface integral in (27) will not reduce to the form in (2). For a sufficiently large number of terms in the series for ψ and χ , (2) and (27) will differ by very little. We shall use (2) with the approximation (4) because it is the simpler expression. For the metallic case $\text{grad } \chi = 0$ and similar remarks can be made concerning the relation between (2) and (26).

4. Interpretation of Potential and Energy Functions.

We should first explain the manner in which the first pair of terms in (7) deviate from exact linear superposition. The latter condition would hold if $A = Qe^{\tau}/D(1 + \tau)$, but this is not identical with the form (9) when $\alpha = 0$, assumed for the first approximation. If this former expression for A is chosen, then the total charge in the overlapping ionic atmospheres will no longer be $-2Q$, but rather less in magnitude and it is necessary to apply Gauss' theorem to preserve this condition. Under linear superposition the charge of one ionic atmosphere will be

** The five conditions obtained from (23) and (25) are,

$$\overline{\Psi}_3 = \frac{1}{2} \int_{-1}^{+1} \Psi_3(\mu_1) d\mu_1 = \frac{1}{2} \int_{-1}^{+1} X_3(\mu_1) d\mu_1 = B_0, \quad (I)$$

$$\int_{-1}^{+1} \mu_1 \Psi_3(\mu_1) d\mu_1 = \int_{-1}^{+1} \mu_1 X_3(\mu_1) d\mu_1 = \frac{2}{3} B_1 a, \quad (II)$$

$$\int_{-1}^{+1} \mu_1^2 \Psi_3(\mu_1) d\mu_1 = \int_{-1}^{+1} \mu_1^2 X_3(\mu_1) d\mu_1 = \frac{2}{3} (B_0 + \frac{2}{3} B_2 a^2), \quad (III)$$

$$D \int_{-1}^{+1} \mu_1 \left(\frac{\partial \psi_3}{\partial r_1} \right)_{r_1=a} d\mu_1 = D' \int_{-1}^{+1} \mu_1 \left(\frac{\partial \chi_3}{\partial r_1} \right)_{r_1=a} d\mu_1 = \frac{2}{3} B_1 D', \quad (IV)$$

$$\frac{2}{3} \frac{Q}{a^2} + D \int_{-1}^{+1} \mu_1^2 \left(\frac{\partial \psi_3}{\partial r_1} \right)_{r=a} d\mu_1 = D' \int_{-1}^{+1} \mu_1^2 \left(\frac{\partial \chi_3}{\partial r_1} \right)_{r=a} d\mu_1 = \frac{2}{15} B_2 D' a^3. \quad (V)$$

For the second approximation ($\lambda_2 = B_2 = 0$) we use the conditions (I), (II) and (IV) to determine the three coefficients λ_1, B_0 and B_1 ($\chi = \chi_2, \Psi = \Psi_2$). The first approximation yields the same result as for the metallic particles since we need only determine A . Indeed provided we apply Gauss' theorem the first approximation will be independent of the particular set of boundary conditions chosen.

allowed to penetrate into the interior of the other particle, which, of course, cannot occur.

It is possible to interpret the second pair of terms in (7), denoted by ϕ_1 , in the following manner. Suppose we seek a solution of the Debye-Hückel equation (1) which vanishes at infinity and such that at the origin $r_1 = 0$ of particle O_1 , the potential tends to that of a dipole of moment m in a medium of dielectric constant D , i.e. $\psi \rightarrow m \cos \theta_1 / Dr_1^2$ as $r_1 \rightarrow 0$. The solution is readily found to be,

$$\psi = \frac{m\kappa}{D} \cos \theta_1 \cdot \left(1 + \frac{1}{\kappa r_1}\right) \cdot \frac{e^{-\kappa r_1}}{r_1}.$$

On comparison with (7) this suggests that the polarisation of the ionic atmospheres accounted for by the second pair of terms in (7) is equivalent to removing the two particles and replacing them by two dipoles of strength, $m = AD\lambda_1/\kappa$.

These dipoles, which lie on the line O_1O_2 will be directed towards or away from each other according as λ_1 is positive or negative. The sign of λ_1 may be determined by treating the particle O_1 under the influence of an external homogeneous electric field, represented by the potential $E r_1 \cos \theta_1 + C$ the field acting in the direction O_2O_1 . The potential is readily found to be,

$$\psi = \frac{Qe^{\epsilon\tau}}{D(1+\tau)} \cdot \frac{e^{-\kappa r_1}}{r_1} \left\{1 + \lambda_1 \cos \theta_1 \left(1 + \frac{1}{\kappa r_1}\right)\right\} + E r_1 \cos \theta_1 + C,$$

where in the insulating case,

$$\lambda_1 = \frac{(D - D') \tau a^2 E}{Q \cdot \left\{ \frac{2 + 2\tau + \tau^2}{1 + \tau} + \frac{D'}{D} \right\}}, \quad (28)$$

$$\text{and in the metallic case,} \quad \lambda_1 = -\frac{D\tau a^2 E}{Q}. \quad (29)$$

We see that, provided $D > D'$, which is true for all sols, $\lambda_1 > 0$ in the insulating case; $\lambda_1 < 0$ in the metallic case.

Physically we can readily understand the reasons for the opposite sign of λ_1 in the two cases. With insulating particles the charge distribution on the surface of the particle remains unchanged and the distortion occurs in the outer layer only. Consider a positively charged particle, so that the outer diffuse layer is negatively charged. The imposed field E will produce an increase of negative charge on the side of O_1 nearest to O_2 and a decrease on the other side. This shift in charge could also be produced by a dipole at the centre of O_1 , directed towards O_2 , so that here $\lambda_1 > 0$. For a metallic particle there is also a diminution of positive charge on the surface of O_1 on the side nearest to O_2 . This will counteract the polarisation produced on the ionic atmosphere by the external field and there will be a resultant accumulation of negative charge in the atmosphere on the side in question. This is to be expected since the metallic surface is far more polarisable than the diffuse layer. The resultant equivalent dipole is found to be directed away from O_2 so that $\lambda_1 < 0$.

Instead of considering O_1 under the influence of the external field E , we can bring it into the field of O_2 . Since this latter field is also directed from O_2 to O_1 , we may again expect $\lambda_1 > 0$ in the insulating case and

$\lambda_1 < 0$ in the metallic case. A new factor enters here, however. When the two ionic atmospheres overlap they tend to repel one another. This effect leads to a diminution in the negative charge density in the region between the two particles. This increases the magnitude of $\lambda_1 (< 0)$ in the metallic case and decreases $\lambda_1 (> 0)$ in the insulating case.

It is possible to speak of an effective polarisability of a colloidal particle with its ionic atmosphere. When the particles are far apart then the potential at the centre of O_1 due to O_2 will be very nearly $Ae^{-\kappa R}/R$ and the electric intensity

$$E = \frac{A}{R^2} (1 + \kappa R) e^{-\kappa R} \approx \frac{A\kappa e^{-\kappa R}}{R}.$$

The polarisability will be proportional to $\lim_{R \rightarrow \infty} \lambda_1/E = \lambda_1 R e^{\kappa R}/A\kappa$ which suggests that $\lambda_1 \rightarrow C e^{\kappa R}/R$ as $R \rightarrow \infty$. The form of the constant C will depend on the boundary conditions chosen.

In a similar fashion we can relate the third pair of terms in (7) to an equivalent quadrupole moment and in general the $N + 1$ th pair of terms in the infinite series for the electric potential to induced electric moments of the N th order.

It is possible to construct simple pictures analogous to those suggested for the electric potential, for each of the terms in the expression or the interaction energy. However, there is no need to do this in detail and we shall only give an elementary and approximate method of calculating the energy, which reproduces qualitatively all the essential characteristics of the more exact results and which reduces to the first approximation under certain conditions.

Let us suppose that as the two particles approach one another, the spherically symmetrical distributions of charge on their surfaces and in their ionic atmospheres remain undistorted. We shall neglect the resulting presence of charge from the diffuse layers inside the interior of the two particles. The potential in the double layer of particle O_1 only will be denoted by $\psi_0^{(1)} = \{Q e^{\tau}/D(1 + \tau)\} e^{-\kappa r_1}/r_1$ and the charge density by $\rho_0^{(1)} = -(D/4\pi) \nabla^2 \psi_0^{(1)} = -(D/4\pi) \cdot \kappa^2 \psi_0^{(1)}$. The two corresponding quantities for the particle O_2 will be denoted by $\psi_0^{(2)}$ and $\rho_0^{(2)}$. Finally the surface density of charge on each particle is $\sigma = Q/4\pi a^2$.

We first attempt to calculate the energy required to bring particle O_1 (without its ionic atmosphere) into the field of O_2 . This is given by

$$\begin{aligned} \int_{S_1} \sigma \psi_0^{(2)} dS_1 &= \frac{Q}{4\pi a^2} \cdot \frac{Q e^{\tau}}{D(1 + \tau)} 2\pi a^2 \int_0^\pi \frac{e^{-\kappa r_2}}{r_2} \sin \theta_1 d\theta_1 \\ &= \frac{Q^2 e^{\tau}}{2DRa(1 + \tau)} \int_{R-a}^{R+a} e^{-\kappa r_2} dr_2 = \frac{Q^2 \delta_2}{Da(1 + \tau)}, \quad (30) \end{aligned}$$

where $\sin \theta_1 d\theta_1 = r_2 dr_2/Ra$, the transformation from θ_1 to r_2 being given by the relation $\cos \theta_2 = (R^2 + a^2 - r_2^2)/2Ra$. The first approximation to the repulsive contribution to the energy, $F_r^{(1)} = (Q^2/Da) f_r^{(1)}(s, \tau)$ reduces to (30) if we put $\delta_1 = 0$, *i.e.* if we neglect Gauss' theorem, which accounts for the conservation of charge. In practice (30) is quite satisfactory, provided $\delta_1 \ll \delta_2$, which holds when $\tau \ll 1$.

The next step is to compute the energy required to bring the ionic atmosphere of O_1 into the field of O_2 . This is given by,

$$\begin{aligned} \int_V \psi_0^{(2)} \rho_0^{(1)} dv &= -\frac{D\kappa^2}{4\pi} \int_V \psi_0^{(2)} \psi_0^{(1)} dv \\ &= -\frac{D\kappa^2}{4\pi} \frac{Q^2 e^{2\tau}}{D^2(1+\tau)^2} \int_V \frac{e^{-\kappa(r_1+r_2)}}{r_1 r_2} dv = -\frac{Q^2 \kappa}{2D(1+\tau)^2} \delta_{00}^{(111)}, \quad (31) \end{aligned}$$

where $\delta_{00}^{(111)}$ is given in (17).

It is readily seen that the first approximation for the attractive contribution to the energy, $F_a^{(1)}(s, \tau) = (Q^2/Da) \cdot f_a^{(1)}(s, \tau)$, reduces to (31) provided we put $\delta_1 = 0$ and also add on the integral of $2\psi_0^{(1)2}$ taken inside the particle O_2 (or that of $2\psi_0^{(2)2}$ inside O_1).

Adding (30) and (31), we get the resultant form for the interaction energy

$$\begin{aligned} F^* &= \frac{Q^2}{Da} f^*(s, \tau) = \frac{Q^2}{Da(1+\tau)} \cdot \left(\delta_2 - \frac{\tau}{2(1+\tau)} \cdot \delta_{00}^{(111)} \right) \\ &= \frac{Q^2}{2Da} \cdot \frac{e^{-\tau(s-2)}}{\tau(1+\tau)^2 s} (1 - e^{-2\tau} - \tau^2 \cdot s - 2), \quad (32) \end{aligned}$$

which is quite accurate, provided $\delta_1 \ll \delta_2$ and $\delta_{00} \approx \delta_{00}^{(111)}$, both conditions holding when $\tau \ll 1$. When $s \rightarrow \infty$, the expression (32) tends to the same limiting value as the true energy, namely,

$$-\frac{Q^2}{2Da} \cdot \frac{\tau}{(1+\tau)^2} \cdot e^{-\tau(s-2)}.$$

This common asymptotic form for $F_2^1 - 2F_1$ and F^* is to be expected since the linear superposition of the charge distributions must be approached more and more as the particles are separated. The energy function (32) has a zero when

$$s_0^* = 2 + \frac{1 - e^{-2\tau}}{\tau^2} \quad (33)$$

and a minimum when

$$s_{\min}^* = \frac{1}{2}b(1 + \sqrt{1 + 4/b\tau}), \quad b = \frac{1}{\tau^2}(1 - e^{-2\tau} + 2\tau^2). \quad (34)$$

When $\tau \ll 1$, $s_0^* \approx 2/\tau$, $s_{\min}^* \approx (1 + \sqrt{3})/\tau$ and when $\tau \gg 1$, $s_0^* \approx 2 + 1/\tau^2$ and $s_{\min}^* \approx 2 + 1/\tau$ (of course $s_0^* \leq s_{\min}^*$). In Table I, we have compared s_{\min}^* and $f^*(s_{\min}^*, \tau)$ with the values of s'_{\min} and $f_1(s'_{\min}, \tau)$ (first approximation). It is seen that the difference is not large, particularly for small τ . We have also included in Table I the values of $f^*(2, \tau)$ (contact) which should be compared with $f_1(2, \tau)$ given in Table VIII in the following paper. It is observed that the two functions are comparable only for small τ , the difference increasing with τ . Thus, when $\tau \ll 1$, $f^*(2, \tau) = \frac{1}{2}(1 - 3\tau + \dots)$, the same form as for $f_1(2, \tau)$. However, when $\tau \gg 1$, $f^*(2, \tau) \approx 1/4\tau^3$ whereas $f_1(2, \tau) \approx 1/16\tau^2$.

It is instructive to point out the essential difference between the forms of the repulsive and attractive terms at large distances. If we imagined the charge Q to be concentrated at the centre of the particle in a potential field proportional to $Qe^{-\kappa R}/R$, then the energy would be of the form $Q^2 e^{-\kappa R}/R$. This is indeed the case for the repulsive term. However it is not permissible to concentrate the charge $-Q$ of the diffuse ionic atmosphere at the centre of the particle, since the limiting form for the attractive term at large distances is proportional to $Q^2 e^{-\kappa R}$, so that it

predominates over the repulsive term. The interesting and significant feature is the absence of the factor $1/R$. This arises simply because the ionic atmosphere is diffuse and theoretically spread over all space, whereas the charge on the particle is confined to its surface. At large distances the most important contribution to the attractive term and indeed to the complete energy comes from the region lying between the two particles.

The result (32) can also be obtained by considering the electric force acting on any element of charge at a point P situated at distances r_1 and r_2 from the particles (P may either lie in the diffuse layer or on the surface of O_1 , say). The electric intensity at P due to O_2 and its atmosphere is merely Q'/Dr_2^2 , where $Q' = \{Qe^{\tau}/(1+\tau)\}e^{-\kappa r_2}$ ($1+\kappa r_2$) is the charge associated with O_2 and contained within the sphere of radius r_2 . This follows at once from elementary electrostatics. Using this result we can again integrate over the surface of O_1 and the volume of its ionic atmosphere and find the two contributions to the force, attractive and repulsive. This method illustrates the screening effect of the outer layer.

TABLE I.*

τ .	$s^*_{\min.}$	$s'_{\min.}$	$-f^*(s^*_{\min.}, \tau)$ $\times 10^3$.	$-f_1(s'_{\min.}, \tau)$ $\times 10^3$.	$f^*(2, \tau)$.	$2f_0(\tau)$.
0	∞	∞	0	0	$\frac{1}{2}$	1
0.1	27.46	27.53	0.866	0.849	0.375	0.8678
.2	13.92	14.03	1.69	1.65	.295	.7639
.3	9.48	9.61	2.45	2.37	.222	.6805
.5	6.03	6.17	3.78	3.47	.140	.5556
.8	4.21	4.37	4.82	4.20	.0770	.4321
1.0	3.65	3.83	5.17	4.29	.0540	.3750
1.5	2.97	3.13	5.16	4.24	.0253	.2800
2.0	2.67	2.76	4.35	3.81	.0136	.2222
3.0	2.40	2.47	3.40	2.95	.00520	.1563
5.0	2.223	2.259	1.88	1.57	.00139	.09722
7.0	2.155	2.179	1.15	1.02	.000558	.07031
9.0	2.118	2.137	0.776	0.668	.000278	.05500
∞	2	2	0	0	0	0

* In the previous work,¹ $s^*_{\min.}$ and $(Q^2/Da)f_1(s^*_{\min.}, \tau)$, for particular values of Q and a , have been plotted (Fig. 6) as functions of τ , but the actual values given here are more useful.

Throughout this work we have assumed that there is no change in charge on the particles as they approach one another. Actually our results can still be used if Q is a function of the mutual separation, say $Q = Q(s)$ with $Q = Q_0$ at infinite separation ($s = \infty$). It is readily seen that the change in energy on the approach of the two particles will now become

$$\frac{Q^2(s)}{Da} \left\{ f_N(s, \tau) - 2 \left(\frac{Q_0^2}{Q^2(s)} - 1 \right) f_0(\tau) \right\} \quad (35)$$

where $f_0(\tau)$ is defined in (3) and N (1, 2 or 3) represents the approximation used. In a recent paper, Langmuir[†] has suggested that the electrical forces associated with colloidal particles are of an attractive nature.

† We are greatly indebted to Dr. J. J. Bikerman for detailed discussions on Langmuir's paper.

In order to have repulsion between the particles he assumes that the ζ potential must remain constant, *i.e.*, the charge is reduced on mutual approach of the particles. However, according to (35), if $Q(s) < Q_0$ then the mutual repulsion at small distances is actually diminished. Further, there is considerable evidence that when electrolyte is added to a sol, the charge on the particle need not change. This suggests that $Q(s) \approx Q_0$, *i.e.*, is practically independent of s . One can estimate the effect of a reduction on the charge by computing the ratio $2f_0(\tau)/f_1(2, \tau)$ using Table I and Table VIII in the following paper. We obtain, for example, the values 2, 5, 5, 28 and 56 when $\tau = 0, 1, 5$ and 9 respectively. Thus, particularly for large τ , a small reduction in charge leads to a large decrease in the interaction energy. For example, for $\tau = 5$ (35) becomes zero when $Q(2)/Q_0 = 0.983$. As s increases (separation of the particles) $f_N(s, \tau)$ decreases rapidly, implying that $Q(s)$ tends to Q_0 very quickly. In addition to (35) we shall also need to compute the energy of adsorption of the ions on the particle surface, complicating matters a great deal. In general, it seems quite difficult to obtain the form of $Q(s)$ and we are compelled to neglect it at present.

5.† Analysis of Work of Langmuir* and Derjaguin.

We wish to discuss those points in the recent papers of Langmuir³ and Derjaguin⁴ on the forces between colloidal particles which have a direct bearing on our work. Since they consider two parallel plates we shall apply our method to this case. The solution given by Derjaguin for (1), which becomes

$$d^2\psi/dx^2 = \kappa^2\psi, \quad . \quad . \quad . \quad . \quad (1i)$$

$$\psi = \zeta \cosh \kappa x / \cosh (\kappa R/2), \quad . \quad . \quad . \quad . \quad (36)$$

where the x axis is taken normal to the plates, the origin being midway and ζ is the potential of the surface of the plates, at distance R apart. The electrical energy per unit area of the plates, corresponding to (2), is

$$-\frac{D\kappa^2}{8\pi} \int_{-R/2}^{R/2} \psi^2 dx + \sigma\zeta = \frac{D\kappa^2\zeta}{4\pi} \left\{ -\frac{\sinh \kappa R + \kappa R}{4 \cosh^2 (\kappa R/2)} + \tanh (\kappa R/2) \right\}, \quad (37)$$

$$\text{where} \quad \sigma = (D/4\pi)(d\psi/dx)_{x=R/2} = (D\kappa\zeta/4\pi) \tanh (\kappa R/2) \quad . \quad (38)$$

is the surface charge density on the plates. Subtracting the limiting form of (37) at infinite separation ($D\kappa^2\zeta/8\pi$) and assuming with Derjaguin that ζ is constant, independent of R , we obtain for the work required to bring the plates together

$$F_\zeta = \frac{D\kappa^2\zeta^2}{16\pi} \left(\frac{\sinh \kappa R - \kappa R}{\cosh^2 (\kappa R/2)} - 2 \right), \quad . \quad . \quad . \quad (39)$$

as is readily verified. On the other hand, if we assume σ is constant, which corresponds to our treatment of two spherical particles, we obtain in place of (39)

making use of (37) and (38). In both cases the energy is always negative, decreasing in magnitude with increasing R . In the first case a minimum is attained at $R = 0$ ($dF_\zeta/dR = 0$).

$$F_\sigma = \frac{\pi\sigma^2}{D\kappa} \left(\frac{\sinh \kappa R - \kappa R}{\sinh^2 (\kappa R/2)} - 2 \right), \quad . \quad . \quad . \quad (40)$$

† Sections 5 and 6 were added in the proof (July 7).

* We are greatly indebted to Dr. J. J. Bikerman for detailed discussions on Langmuir's paper.

It is convenient to discuss the work of Langmuir and Derjaguin together. Langmuir's method is the same as that described by Fowler,[†] who considers electron atmospheres, and we shall quote the argument of the latter. If ν_0 is the concentration of electrons (ions) at the median plane ($x = 0$), ν_a that at the surface of the plates ($x = \pm R/2$), then the electrical negative force (directed inwards between the two plates) acting on unit area of the inner surface of each plate is

$$kT(\nu_a - \nu_0) = \frac{2\pi\sigma^2}{D} = \frac{D\xi^2\kappa^2}{8\pi} \tanh^2(\kappa R/2). \quad (41)$$

Derjaguin uses this result, considers the analogous force acting on the outer surfaces of the plates and then finds the resultant force which is repulsive and which leads to the energy term $(D\kappa\xi^2/4\pi)(1 - \tanh(\kappa R/2))$. This is exactly equal but opposite in sign to that term in (39) which is associated with the plates only, namely $(\sigma - \sigma_0)\xi$, where $\sigma_0 = D\kappa\xi/4\pi$ is the surface charge density at infinite separation. The explanation for this is that we have only considered the force on the inner sides of the plates, subtracting a constant contribution to this force, namely that acting at $R = \infty$, and this is actually opposite in sign to that calculated by Derjaguin. It is not at all necessary to consider the forces acting on the outer surfaces because they are balanced by the forces acting on their diffuse ionic layers.* This is so since there is no change in energy associated with the outer surfaces and their ionic atmospheres when the plates are brought together. Derjaguin neglects the forces acting on the ionic atmospheres[†] and the fact that he obtained a repulsion, whereas our method yields an attraction, leads us to the opinion that his results are incorrect.[‡]

On the other hand, Langmuir considers the force (41) and introduces a positive pressure on the plates due to the osmotic forces (transport of momentum according to Fowler) which he puts equal to $kT\nu_a$, so

[†] R. H. Fowler, *Statistical Mechanics*, 2nd ed., 1936, p. 366 (Camb. Univ. Press). Langmuir works with the complete Debye-Hückel equation and not with (1 i), but we are chiefly concerned here with the general principles.

* A similar remark can be made concerning Langmuir's use of the osmotic pressure on the outer sides of the plates.

[†] Both Derjaguin and Langmuir calculate the force rather than the energy. This is quite legitimate, of course, but one must be careful to show that the forces considered actually perform the total work done in bringing the plates together. In our opinion, there is less danger of confusion by working directly with the (free) energy. In cataphoresis, where we examine the motion of a particle in an external electric field, we consider not only the force on the particle itself but also that on its ionic atmosphere, yielding two terms. In an analogous fashion, we have two terms in the expression for the force (and energy) between two particles.

[‡] Derjaguin's expression for the mutual energy is $(D\xi^2a/2) \ln(1 + e^{-\tau(s-2)})$, in our notation, reducing to $D\xi^2a \ln 2/2$ at $s = 2$, which may be compared with our result $D\xi^2a(1 + \tau)^2 f_1(2, \tau) \approx D\xi^2a/16$ for $\tau \gg 1$ (see Table II in the following paper). We also take exception to his method of passing from the case of parallel plates to that of spherical particles. He assumes that the mutual energy can be expressed as a surface integral over each particle (see his equation (19), p. 165), whereas, according to (2), a volume integral should also be included. For two parallel plates, these two integrals can be combined into one surface integral. Derjaguin is careful to state that his method is valid when $\tau \gg 1$ and the particles are close together, in which case the approximation of two plates would appear to be reasonable. However, our calculations show that two plates attract one another, implying that sols consisting of large particles are unstable, which is not so. Thus the "end effects" which have been neglected and which are due to the finite curvature of the particles seem to be of decisive importance. Neither our method nor that of Derjaguin succeeds in treating adequately the case $\tau \gg 1$.

that the net (repulsive) pressure on the plates is $kT\nu_0$. This procedure is legitimate, provided the plates are permeable to water which all passes through the plates and not around their edges when the latter are moved together (piston arrangement). This is certainly not the case in actual sols (*e.g.*, Schiller layers).

Although there is little resemblance between Langmuir's osmotic term and our energy contribution from the ionic atmospheres § it is possible to connect the two in the following manner. Debye calculated the deviation of the osmotic pressure from the ideal law for a true electrolyte by considering the free energy of charging the ions. In a similar fashion the change in free energy associated with charging the ionic atmospheres, as a result of bringing the plates together from infinity, can be equated to the corresponding work done by the osmotic forces. (No work would be done by the osmotic forces when the ions are uncharged since there is no change in volume.) Thus, if a given number of ions occupy a volume ΔV_0 when $R = \infty$ and a volume ΔV for a distance R between the plates, then the work done by them is $\int_{\Delta V_0}^{\Delta V} p dv$, where p is the osmotic pressure, and we need to sum over all volume elements in the diffuse layers. Hence the contribution from the osmotic forces will be included in the free energy of charging the ions and particles and this has effectively been taken into account in our method for sufficiently dilute sols.

For concentrated sols (*e.g.*, in tactoids, Schiller layers, coacervates, etc.) it is questionable whether the average electrical energy (calculated by us) and the free energy will be almost the same. However, it seems reasonable to suppose that the two quantities, average energy and free energy, behave in a similar fashion with respect to variation in the particle distance, *i.e.*, if a minimum is exhibited in one it will also occur in the other (compare the theorem that the average energy is $3/2$ ths of the free energy in the approximate Debye-Hückel theory).

We conclude that Langmuir's method of introducing the osmotic forces is incorrect and the appropriate calculation suggested above would be just as difficult as the one carried out in our treatment of the ionic atmospheres. Apparently the case of parallel plates (infinite) does not reveal the essential characteristics in the form of the mutual energy of colloidal particles. In actual sols consisting of plate-like particles, for example, the finite size of the particles, comparable with their mutual separation, should play an important role in determining the nature of the electrical forces and hence it is doubtful whether Langmuir's example will apply. In a further report we shall consider the case of infinite parallel cylindrical particles.

6. Relation Between Energy of Two Particles (Ions) and the Debye-Hückel Equation.

The relation of our results to the basic assumptions in the Debye-Hückel theory is of some significance. The Poisson-Boltzmann equation for the potential $\psi_j(r)$ in the vicinity of an ion j is

$$\nabla^2 \psi_j(r) = - \frac{4\pi}{D\mathcal{V}} \sum_i N_i e_i \exp(-V_{ij}(r)/kT), \quad (42)$$

§ Langmuir's osmotic term is always positive (repulsive), whereas the term in (39) arising from the diffuse layers is positive at small R and negative at large R . The corresponding term in (40) is negative for all R .

where N_i is the number of ions of type i , charge e_i in the solution of volume V , and $V_{ij}(r)$ is the potential of the mean force acting on ion i at distance r from ion j and is given by

$$\exp(-V_{ij}(r)/kT) = \frac{\int \dots \int \exp(-E/kT) dv_1 \dots dv_{N-1}}{\int \dots \int \exp(-E/kT) dv_1 \dots dv_{N-2}} \quad (43)$$

where E is the Coulomb (and van der Waals) interaction energy associated with all the ions ($N = \sum_i N_i$ in number). In the integral in the numerator in (43), ions i and j are fixed at distance r , whereas in the denominator ion i moves over the volume V . Both these integrals yield free energies** of charging all the ions, one for i and j fixed, the other for j fixed. In the latter case, since the probability of ion i being in the vicinity of j is of the order $1/N$, we may assume that ion i is also fixed at large distance from j and account for its motion by a multiplicative factor V . Hence $V_{ij}(r)$ is the difference in the free energy of charging all the ions obtained by first fixing i and j at distance r and then at infinite separation. We have attempted to show in one of the earlier papers¹ that this quantity was actually evaluated for two colloidal particles. In the case of two ions the corresponding result is admittedly approximate, since we are inconsistent when we use the Debye-Hückel equation to find V_{ij} .

Debye and Hückel put $V_{ij} = e_i e_j \approx e_i e_j \exp(-\kappa r)/Dr$, which corresponds to the repulsive term $f_r(s, \tau)$ in our energy expression and the attractive term $f_a(s, \tau)$ has been entirely omitted in their theory. (This refers to two ions of like charge; for ions of opposite charge f_r would be attractive and f_a repulsive.) However, the following discussion shows that this neglect is quite legitimate in very dilute electrolyte solutions ($\tau \ll 1$), where the Debye-Hückel theory is valid. Firstly, according to Table I in the following paper, the ratio of the attractive to the repulsive terms at contact of the ions (particles) is

$$f_a(2, \tau)/f_r(2, \tau) \approx -\tau,$$

when $\tau \ll 1$. For a 1-1 valency electrolyte at a concentration of $\gamma = 0.0231$ mol./l. with $a = 2 \times 10^{-8}$ cm. (ionic diameter rather than radius), then $\tau = a\sqrt{\gamma}/3.04 \times 10^{-8} = 0.1$ at a temperature $T = 18^\circ \text{C}$. and for two ions of the same sign, the depth of the minimum is

$$(e^2/Da)f_1(s_{\min}, 0.1) = 1.2 \times 10^{-18} \text{ ergs} \approx 0.003 kT,$$

making use of Table I, remembering that $Q = e$, the electronic charge here. Further, the ratios of the separation between the ions at the zero $r_0 = as_0$ and minimum $r_{\min} = as_{\min}$ (in their mutual energy function) to the so-called thickness of the ionic atmosphere $1/\kappa$, are $r_0\kappa \approx 2$ and $r_{\min}\kappa \approx 1 + \sqrt{3}$ respectively. This is obtained by putting $s_0 \approx s_0^* \approx 2/\tau = 2/\kappa a$ and $s_{\min} \approx s_{\min}^* \approx (1 + \sqrt{3})/\tau = (1 + \sqrt{3})/\kappa a$, which holds for small τ . It follows from this example that in dilute solutions the repulsive term is much larger than the attractive one for

** Strictly speaking one should only use this term for a measurable property. However, the implication here is that the mathematical expressions in statistical mechanics for the quantities under consideration correspond to that of a proper free energy.

interionic distances less than the thickness of the ionic atmosphere. For larger concentrations, say $\gamma = 2.31$ mol./l.,

$$\tau = 1, \quad f_a(2, \tau)/f_r(2, \tau) \approx -1/2, \quad r_0\kappa \approx 3, \quad r_{\min.}\kappa \approx 3.8,$$

and the energy at the minimum is $0.015kT$. Although the minimum does not seem to be important at any concentration for a 1—1 type, nevertheless at closer separation between the ions at concentrations of about 1 mol. or greater, the attractive term neglected in the Debye-Hückel theory is of the same order as the positive term. (For ions of opposite charge there will be a maximum at large separations.) For higher valency types the minimum deepens and for two Th ions,⁶ for example, in a 4—1 type of electrolyte, $\tau = 1$ at $\gamma = 0.231$ mol./l. and the energy value at the minimum is $0.24kT$.

Thus our results suggest a serious discrepancy in the Debye-Hückel theory at strong concentrations. Using an integral equation for V_H , Kirkwood⁷ obtained not one maximum (or minimum) but a whole series of them. Of course our theory is only qualitative when applied to true electrolytes, whereas Kirkwood's method is much more rigorous. However, this discussion clearly shows that it is wrong to apply the Debye-Hückel theory of electrolytes to colloidal solutions in such a way that the particles are treated on the same basis as the ions. This discrepancy in the Debye-Hückel theory has a minor effect on our results for two colloidal particles, firstly because the electrolyte concentration in hydrophobic sols is ordinarily below 1/10th molar and secondly on account of the large size of the particles.¹

Summary.

Applying a general formula, which has been developed to calculate the interaction energy of two spherical, hydrophobic colloidal particles, a first, second and third approximation are obtained. The results depend upon the use of the approximate Debye-Hückel equation in the theory of electrolytes. Both metallic and insulating particles have been considered. The first approximation corresponds to undistorted penetration of the double layers, the second to induced effective dipoles, the third to effective quadrupoles and so on. A very simple method of obtaining a rough estimate of the first approximation has been given. This yields all the essential features of the more exact results.

A comparison is made of our theory with those of Langmuir and Derjaguin, whose results are shown to be unsatisfactory. The relation of our work to the basic assumptions in the Debye-Hückel theory is discussed, and it is seen that the negative term in the mutual energy between two particles should also exist for two ions of the same sign. This has been omitted by Debye and Hückel and is negligible for dilute electrolyte concentrations but important at strong concentrations.

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⁶ Cf. Prins, *Trans. Faraday Soc.*, 1937, 33, 110, who detected a "super-arrangement" of Th ions in $\text{Th}(\text{NO}_3)_4$.

⁷ J. G. Kirkwood, *Chem. Rev.*, 1936, 19, 236.

II. NUMERICAL COMPUTATIONS OF ENERGY FUNCTION.

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1. Introduction.

In this paper we shall give the numerical results for the first three approximations to the electrical interaction energy of two hydrophobic colloidal particles. The first two approximations for the metallic case were already computed in the earlier work.¹ Here, we shall also consider insulating particles. Because of the great amount of labour entailed in the calculation of the numerical results we have not carried out a detailed description of the second and third approximations. The energy at contact has been computed for the three approximations and also the variation of the energy with the inter-particle distance for the three particular concentrations of electrolyte. We shall extend the calculations for the first approximation in a later report, treating in particular the properties of the maximum * (including the van der Waals' contribution) and minimum in the energy. There is also included a discussion of the general behaviour of the energy function at large distances of separation.

In the previous papers,¹ the method for determining the coefficients in the potential (for the second approximation in the metallic case) lead to negative values for the energy at contact for large τ . This would imply that large colloidal particles are unstable which is not found to be the case. A better method of calculating these coefficients shows that the energy at contact always remains positive for all three approximations. This is also true for the insulating particles.

The results obtained suggest that, provided τ is less than 5 or 10, the differences between the three approximations are not large. This is encouraging for the following reason. To explain the Schultze-Hardy rule it will be necessary to consider the complete Debye-Hückel equation. In view of the greatly increased mathematical difficulties involved in the treatment of this equation it is fortunate that the following results suggest linear superposition of the solutions for the individual (small) particles to yield a reasonable first approximation. This latter solution has already been obtained for ions by Gronwall, La Mer and Sandved.² We shall report later upon the application of their work to colloidal particles.³

Although the general method, which has been developed, permits the computation of the fourth and higher approximations, for a number of reasons it seems hardly worth while to carry this out at present. Firstly

¹ S. Levine, *Proc. Roy. Soc., A*, 1939, **170**, 145, 165.

* In another paper, appearing shortly, this is carried out and a number of applications are given.

² T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, 1928, **29**, 358.

³ S. Levine, *J. Chem. Physics (in the Press)*.

TABLE I.—LIMITING FORMS AT CONTACT FOR $\tau \ll 1$.

$$\begin{aligned} \delta_1 &= \frac{\tau^2}{6}(1-2\tau+\dots); \quad \delta_2 = \frac{1}{2}\left(1-\tau+\frac{2}{3}\tau^2+\dots\right); \quad \delta_{00} = 2+\tau\left(\frac{3}{4}\ln 3-2\right)+\dots=2-1.1760\tau+\dots; \\ \delta_{01} &= \frac{10}{3}-\frac{5}{8}\ln 3 = 2.6467; \quad \delta_{11} = \frac{1}{16\tau}\left(\frac{19}{3}+\frac{3}{4}\ln 3\right) = \frac{0.4473}{\tau}; \\ \delta_{02} &= \frac{1}{\tau}\left(\frac{93}{160}-\frac{21}{128}\ln 3\right) = \frac{0.4010}{\tau}; \quad \delta_{12} = \frac{1}{128\tau^2}\left(\frac{703}{15}-\frac{3}{4}\ln 3\right) = \frac{0.3597}{\tau^2}; \\ \delta_{22} &= \frac{1}{\tau^2}\left(\frac{18539}{15360}-\frac{45}{4096}\ln 3\right) = \frac{1.1949}{\tau^2}. \\ f_r^{(1)}(2, \tau) &= \frac{1}{2}\left(1-2\tau+\frac{19}{6}\tau^2+\dots\right); \quad f_a^{(1)}(2, \tau) = -\frac{7}{2}(1-3.1760\tau+\dots); \\ f_1(2, \tau) &= \frac{1}{2}(1-3\tau+6.3427\tau^2+\dots). \end{aligned}$$

	Metallic Particles.		Insulating Particles.			
	L.S.M.*		$\varepsilon = 1/80.$	$\varepsilon = 0.05.$	$\varepsilon = 0.10.$	$\varepsilon = 0.15.$
λ'_1	—	0.20787	0.13987	0.13107	0.12007	0.10977
λ_1	—	0.21687	0.15187	0.14137	0.12847	0.11667
λ_2	—	0.0422072	0.0386672	0.0363572	0.0312572	0.0279172
$f_r^{(2)}(2, \tau)$	0.4481	0.83167	0.5350	0.93017	0.5300	0.94527
$f_a^{(2)}(2, \tau)$	—	$\frac{7}{2}(1-4.2577\tau)$	—	$\frac{7}{2}(1-2.4277\tau)$	—	$\frac{7}{2}(1-2.5907\tau)$
$f_2(2, \tau)$	0.4481	1.3327	0.5350	1.4307	0.5300	1.4457
$f_a^{(3)}(2, \tau)$	—	$\frac{7}{2}(1-4.2697\tau)$	—	$\frac{7}{2}(1-2.3267\tau)$	—	$\frac{7}{2}(1-2.5277\tau)$
$f_3(2, 0) = f_r^{(3)}(2, 0)$	0.4489		0.5522	0.5491	0.5438	0.5396

* In these tables, L.S.M. \equiv least square method, M.M. \equiv moment method and P.M. \equiv point method (also in Fig. 4).

the formulæ become more and more complicated as we pass to higher terms in the series for the electric potential. Secondly it is found that at least for small τ , the correction from the higher terms will not be too large. When τ is large, it may be simpler to develop other methods of calculating the energy. Finally we should really use the complete Debye-Hückel equation and also introduce the hydration and electrostrictive effects, and it is desirable to examine this before treating the approximate equation in any greater detail.

In § 2 an explanation is given of the various tables containing the numerical results, in §§ 3 and 4 we discuss the properties of the second and the third approximations respectively.

2. General Discussion of the Numerical Results.

Although the general expressions for the energy functions even at contact ($s = 2$) are fairly complicated, it is possible to obtain simple limiting forms when $\tau \ll 1$ and when $\tau \gg 1$. The first case corresponds to small electrolytic concentrations or small particles, the second case to large electrolytic concentrations or large particles. In Table I we have listed for $s = 2$ and $\tau \ll 1$ the quantities δ_{nm} , $n, m = 0, 1, 2$, λ_1 and λ_2 , and also the various approximations to the energy functions, giving in addition the repulsive and the attractive contributions. In Table II the corresponding expressions for $s = 2$ and $\tau \gg 1$ are given

TABLE II.—LIMITING FORMS AT CONTACT FOR $\tau \gg 1$.

$$\begin{aligned}\delta_1 &= \frac{1}{4\tau} \left(1 - \frac{2}{\tau} + \dots \right); \delta_2 = \frac{1}{4\tau}; \delta_{00} = 1 + \frac{3}{8\tau} + \frac{3}{16\tau^2} + \dots \\ \delta_{01} &= \frac{3}{4\tau}; \delta_{11} = \frac{1}{8}; \delta_{02} = \frac{7}{8\tau}; \delta_{12} = \frac{49}{40\tau}; \delta_{22} = \frac{1}{8} \\ f_r^{(1)}(2, \tau) &= \frac{1}{2\tau^2} \left(1 - \frac{7}{4\tau} + \dots \right); f_a^{(1)}(2, \tau) = -\frac{7}{16\tau^2} \left(1 - \frac{5}{2\tau} + \dots \right); \\ f_1(2, \tau) &= \frac{1}{16\tau^2} \left(1 + \frac{7}{2\tau} + \dots \right).\end{aligned}$$

	Metallic Particles.			Insulating Particles, any s .
	P. M.	M. M.	L. S. M.	
λ'_1	$-\frac{1}{3}$	$-\frac{3}{4\tau}$	$-\frac{9}{8\tau}$	$\frac{3}{4\tau}$
λ_1	$-\frac{3}{11}$	$-\frac{3}{4\tau}$	$-\frac{9}{8\tau}$	$\frac{3}{4\tau}$
λ_2	$-\frac{2}{11}$	$-\frac{5}{4\tau}$	$-\frac{15}{8\tau}$	$\frac{5}{4\tau}$
$f_r^{(2)}(2, \tau)$	$\frac{1}{3\tau^2}$	$\frac{1}{2\tau^2} \left(1 - \frac{5}{2\tau} \right)$	$\frac{1}{2\tau^2} \left(1 - \frac{23}{8\tau} \right)$	$\frac{1}{2\tau^2} \left(1 - \frac{1}{\tau} \right)$
$f_a^{(2)}(2, \tau)$	$-\frac{1}{54\tau}$	$-\frac{7}{16\tau^2} \left(1 - \frac{4}{\tau} \right)$	$-\frac{7}{16\tau^2} \left(1 - \frac{257}{56\tau} \right)$	$-\frac{7}{16\tau^2} \left(1 - \frac{4}{7\tau} \right)$
$f_2(2, \tau)$	$-\frac{1}{54\tau}$	$\frac{1}{16\tau^2} \left(1 + \frac{8}{\tau} \right)$	$\frac{1}{16\tau^2} \left(1 + \frac{73}{8\tau} \right)$	$\frac{1}{16\tau^2} \left(1 - \frac{4}{\tau} \right)$
$f_r^{(3)}(2, \tau)$	$\frac{3}{11\tau^2}$	$\frac{1}{2\tau^2} \left(1 - \frac{15}{4\tau} \right)$	$\frac{1}{2\tau^2} \left(1 - \frac{19}{4\tau} \right)$	$\frac{1}{2\tau^2} \left(1 + \frac{1}{4\tau} \right)$
$f_a^{(3)}(2, \tau)$	$-\frac{19}{1210\tau}$	$-\frac{7}{16\tau^2} \left(1 - \frac{68}{7\tau} \right)$	$-\frac{7}{16\tau^2} \left(1 - \frac{739}{84\tau} \right)$	$-\frac{7}{16\tau^2} \left(1 + \frac{18}{7\tau} \right)$
$f_3(2, \tau)$	$-\frac{19}{1210\tau}$	$\frac{1}{16\tau^2} \left(1 + \frac{38}{\tau} \right)$	$\frac{1}{16\tau^2} \left(1 + \frac{283}{12\tau} \right)$	$\frac{1}{16\tau^2} \left(1 - \frac{16}{\tau} \right)$

In a similar fashion quite simple expressions are obtained for δ_{nm} , λ_1 and λ_2 and also for the energy functions when s is sufficiently large (Table III). From an examination of these tables, the details of which are found in the following sections, many important and interesting properties of the interaction energy can be derived.

In Tables IV to VIII we have calculated the values of δ_{nm} , λ_1 , λ_2 and the energy for the three approximations, when the particles are in

TABLE III.—LIMITING FORMS AT LARGE SEPARATIONS ($s \gg 2$).

$$\begin{aligned}\delta_1 + \delta_2 &= \frac{e^{-\tau(s-2)}}{s(1+\tau)}, \quad \delta_{00} \approx 1 + \frac{e^{-\tau(s-2)}}{s\tau} (1 - e^{-2\tau} + \tau s - 2), \\ \delta_{01} &\approx 2\delta_{02} \approx 2e^{-\tau(s-2)}, \quad \delta_{11} \approx \frac{1}{3} \left(1 + \frac{2}{\tau}\right), \quad \delta_{12} \approx \frac{27}{20} e^{-\tau(s-2)}, \\ \delta_{22} &\approx \frac{1}{5} \left(1 + \frac{6}{\tau} \left(1 + \frac{1}{\tau}\right)^2\right), \quad \lambda_1' \approx \lambda_1 \sim \frac{e^{-\tau(s-2)}}{s} \sim \lambda_2 \\ f_r^{(1)}(s, \tau) &= \frac{e^{-\tau(s-2)}}{s(1+\tau)^2}, \quad f_a^{(1)}(s, \tau) \approx -\frac{\tau}{(1+\tau)^2} \frac{e^{-\tau(s-2)}}{s} \left(\frac{1}{1+\tau} + s - 2\right) \\ f_1(s, \tau) &\approx \frac{e^{-\tau(s-2)}}{s(1+\tau)^2} \left(\frac{1}{1+\tau} - \tau s - 2\right) \\ f_2(s, \tau) - f_1(s, \tau) &\approx f_a^{(2)}(s, \tau) - f_a^{(1)}(s, \tau) \approx -\frac{\tau\lambda_1'}{(1+\tau)^2} \delta_{01} = -\frac{e^{-2\tau(s-2)}}{s} \alpha_1(\tau) \\ f_r^{(2)}(s, \tau) - f_r^{(1)}(s, \tau) &\approx \frac{\delta_1 + \delta_2 \lambda_1'}{1+\tau} \approx \frac{e^{-2\tau(s-2)}}{s^2} \frac{\alpha_1(\tau)}{2\tau} \\ f_3(s, \tau) - f_2(s, \tau) &\approx f_a^{(3)}(s, \tau) - f_a^{(2)}(s, \tau) \approx -\frac{\tau\lambda_2}{(1+\tau)^2} \delta_{02} \approx \frac{e^{-2\tau(s-2)}}{s} \alpha_2(\tau) \\ f_r^{(3)}(s, \tau) - f_r^{(2)}(s, \tau) &\approx \frac{\delta_1 + \delta_2 \lambda_2}{1+\tau} \approx \frac{e^{-2\tau(s-2)}}{s^2} \frac{\alpha_2(\tau)}{\tau}\end{aligned}$$

τ .		0.	0.1.	0.5.	1.	2.	7.	9.	$\gg 1$.
Metallic case	$-\alpha_1(\tau)$	0	0.00136	0.0460	0.102	0.117	0.0556	0.0240	$3/\tau^2$
M.M. or L.S.M.	$-\alpha_2(\tau)$	0	0.23	0.3601	0.0470	0.163	0.0210	0.0128	$5/2\tau^2$
Insulating case	$\alpha_1(\tau)$	0	0.3584	0.193	0.427	0.281	0.367	0.189	$3/\tau^2$
$\epsilon = 0, 10$	$\alpha_2(\tau)$	0	0.633	0.338	0.0262	0.0875	0.134	0.0958	$5/2\tau^2$

TABLE IV.—NUMERICAL VALUES OF δ_{nm} 's AT CONTACT.

τ .	δ_{00} .	δ_{01} .	δ_{11} .	δ_{02} .	δ_{12} .	δ_{22} .
0.0	2.0	2.6467	∞	∞	∞	∞
0.1	1.8916	1.0499	5.3301	5.5407	63.329	1499.5
0.3	1.7200	0.8948	2.3177	1.6846	8.3332	66.883
0.5	1.5924	0.7768	1.6818	1.0434	3.4014	18.481
0.8	1.4560	0.6388	1.2930	0.7185	1.8971	7.1761
1.0	1.3900	0.5686	1.1498	0.6052	1.4719	4.7858
2.0	1.2112	0.3533	0.8098	0.3545	0.6915	1.8131
3.0	1.1391	0.2486	0.6672	0.2560	0.4675	1.1580
5.0	1.0808	0.1525	0.5394	0.1680	0.2670	0.7415
7.0	1.0560	0.1092	0.4819	0.1181	0.1861	0.5737
9.0	1.0437	0.08478	0.4487	0.09469	0.1538	0.4848
∞	1.0000	0	0.3333	0	0	0.3488

contact. In Figs. 1, 2, and 3 we plot the variation of the energy with the inter-particle distance for three particular values of τ , namely 1/2, 2 and 5 respectively. These three values of τ have been chosen because they are fairly evenly distributed with respect to the energy scale ($f_1(2, 0.5)/f_1(2, 2) \approx 7.0$, $f_1(2, 2)/f_1(2, 5) \approx 6, 3$).

Instead of giving the actual value of the energy it is more useful to compute the functions $f_r^{(N)}(s, \tau)$, $f_a^{(N)}(s, \tau)$ and $f_N(s, \tau)$ where $N = 1, 2$ and 3 for the first, second and third approximations respectively. These

TABLE VI.—REPUISIVE CONTRIBUTION TO ENERGY (f_r) AT CONTACT.

τ .	$f_r^{(1)}(2, \tau) \times 10.$	Metallic particles.			Insulating particles.	
		P.M.	L.S.M.		$\epsilon = 0.10.$	
			$f_r^{(2)}(2, \tau) \times 10.$	$f_r^{(3)}(2, \tau) \times 10.$	$f_r^{(2)}(2, \tau) \times 10.$	$f_r^{(3)}(2, \tau) \times 10.$
0	5.0	4.4231	4.4810	4.4889	5.3000	5.4383
0.1	4.1381	3.5700	3.6282	3.5737	4.4340	4.5315
0.3	2.9843	2.4622	2.5284	2.4947	3.2439	3.4009
0.5	2.2613	1.8040	1.8606	1.8046	2.4871	2.6134
0.8	1.5883	1.2185	1.4377	1.3741	1.7551	1.8779
1.0	1.2938	0.9736	1.0339	0.9777	1.4319	1.5453
2.0	0.5811	.4151	0.4660	.4167	0.6472	0.7123
3.0	.3262	.2282	.3199	.2436	.3613	.4024
5.0	.1437	.09874	.1236	.10996	.1567	.1730
7.0	.08028	.05472	.07073	.06310	.08631	.09555
9.0	.05114	.03469	.04597	.04172	.05438	.05928

TABLE VII.—ATTRACTIVE CONTRIBUTION TO ENERGY (f_a) AT CONTACT.

τ .	$-f_a^{(1)}(2, \tau) \times 10.$	Metallic particles.			Insulating particles.	
		P.M.	L.S.M.		$\epsilon = 0.10.$	
			$-f_a^{(2)}(2, \tau) \times 10.$	$-f_a^{(3)}(2, \tau) \times 10.$	$-f_a^{(2)}(2, \tau) \times 10.$	$-f_a^{(3)}(2, \tau) \times 10.$
0.1	0.3706	0.3516	0.3534	0.3562	0.3811	0.3832
0.3	.6657	.5654	.5767	.5793	.7208	.7409
0.5	.7210	.5503	.5693	.5712	.8126	.8506
0.8	.6696	.4462	.4775	.4753	.7869	.8531
1.0	.6114	.3787	.4162	.4099	.7265	.8107
2.0	.3613	.1862	.2293	.2267	.4587	.5400
3.0	.2258	.1244	.1493	.1302	.2867	.3504
5.0	.1088	.06006	.08752	.06378	.1342	.1612
7.0	.06286	.03961	.04864	.03998	.07526	.09434
9.0	.04124	.02930	.03390	.02752	.04816	.05838

three functions have been defined by equations (12), (13) and (14) respectively in I. We have concentrated on the energy at contact for two reasons; firstly, it is the simplest quantity to compute, and secondly the largest difference between the successive approximations will occur when the particles are close together and hence we shall best be able to judge whether sufficiently rapid convergence is being attained. We shall denote λ_1' as the value of λ_1 for the second approximation (and reserve λ_1 and λ_2 for the third).

TABLE VIII.—RESULTANT ENERGY (f) AT CONTACT.

		Metallic Particles.				Insulating Particles.				
		P.M.	M.M.		L.S.M.		$\epsilon = .05.$	$\epsilon = 0.10.$	$\epsilon = 0.15.$	$\epsilon = 0.10.$
$\tau.$	$f_1(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$	$f_2(z, \tau).$
0.	0.5	0.4423	0.4500	0.4434	0.4481	0.4489	0.5328	0.5300	0.5274	0.5438
0.1	.3768	.3218	.3291	.3100	.3275	.3216	.4084	.4053	.4027	.4148
0.3	.2319	.1897	.1923	.1888	.1952	.1915	.2545	.2523	.2507	.2660
0.5	.1540	.1254	.1310	.1237	.1291	.1233	.1677	.1675	.1668	.1763
0.8	.09187	.07723	.08037	.07493	.09602	.08988	.09665	.09682	.09613	.1025
1.0	.06824	.05949	.06372	.05711	.06178	.05678	.06950	.07055	.06931	.07346
2.0	.02198	.02289	.02372	.02146	.02367	.01900	.01866	.01885	.01905	.01727
3.0	.01004	.01038	.01179	.01084	.01706	.01134	.007338	.007458	.007608	.005201
5.0	.003488	.003868	.004690	.004609	.003611	.004618	.002308	.002245	.002298	.001179
7.0	.001742	.001511	.002150	.001988	.002209	.002312	.001093	.001105	.001122	.001208
9.0	.009897	.005339	.001213	.001397	.001207	.001420	.006268	.006222	.006368	.008841
10.0		.00219								
11.0		.00926								
12.0		—0.4368								

The first approximation has already been examined to some extent in I and II and we need only briefly recall its most important properties. At contact $f_r^{(1)}(2, \tau)$ decreases very rapidly from $1/2$ to 0 as τ goes from 0 to infinity. Over the same range of τ , the negative term $f_a^{(1)}(2, \tau)$ at first decreases from 0 to a minimum value -0.072 at $\tau \approx 0.5$ and then increases again to 0. The resultant function $f_1(2, \tau)$ behaves like $f_r^{(1)}(2, \tau)$, but being always less in magnitude. As a function of distance $f_1(s, \tau)$, for given τ_1 rapidly decreases as s increases, reaching zero at $s = s_0$, where $f_a^{(1)}(s_0, \tau) = -f_r^{(1)}(s_0, \tau)$ and then remains negative for $s > s_0$. At a certain $s_{\min} > s_0$, $f_1(s_{\min}, \tau)$ reaches a minimum and then increases slowly to zero as $s \rightarrow \infty$. The values of s_{\min} and $f_1(s_{\min}, \tau)$ as functions of τ are given in Table I in I.

3. Second Approximation.

We shall first consider the metallic case, for which the second approximation was previously calculated¹ on the assumption that the potential at the two end points on each particle was the same (point method). It turned out that, with the value of λ_1' so obtained, the second approximation became negative for large τ , whereas the first approximation to the energy at contact remained positive. It was thought desirable to calculate λ_1' in the most suitable manner possible to ascertain whether better results could be obtained.

When $s = 2$ (contact) the point method yields,

$$\lambda_1' = -\tau(1 - \frac{1}{3}e^{-2\tau})/\{3(1 + \tau) - \frac{1}{3}e^{-2\tau}(1 + 3\tau)\} \quad (2)$$

According to the moment method described in III,

$$\lambda_1' = -\left(1 + \frac{1}{s\tau}\right) \left/ \left(1 + \frac{2}{s\tau} + \frac{2}{(s\tau)^2} + \frac{1}{3\delta_1}\right) \right., \quad (3)$$

which at contact, becomes

$$\lambda_1' = -(1 + 2\tau) \left/ \left\{2 + 2\tau + \frac{1}{\tau} + \frac{8\tau^2}{3} \frac{\tau + 1}{\{\tau - 1 + (\tau + 1)e^{-2\tau}\}} \right\} \right. \quad (4)$$

The least square method yields a rather complicated expression for λ_1' and the reader is referred to the mathematical paper³ for its exact form. The limiting forms for $\tau \ll 1$, $\tau \gg 1$ and $s \gg 2$ are shown in Tables I, II and III respectively. In all these three methods λ_1' is negative, as was suggested in I.

It is seen from the data in the tables that whereas by the point method λ_1' decreases from 0 to $-1/3\tau$ as τ goes from 0 to ∞ , according to the other two methods λ_1' decreases from zero to a certain minimum value and then increases to zero as $\tau \rightarrow \infty$. Consequently both by the moment and the least square methods the energy at contact for the second approximation remains positive whereas we observe from Table VIII that by the point method, it becomes negative for large τ ($\tau \gtrsim 11, 7$).

There are a number of remarks worthy of mention concerning the behaviour of the energy at contact in the metallic case. Firstly, when $\tau = 0$, $f_2(2, 0) < f_1(2, 0)$. Now, it has been already mentioned^{1*} that when $\tau = 0$, we are dealing with two charged metallic spheres immersed in water, whose mutual energy is

$$(Q^2/Da)\{(1 - \ln 2)/\ln 2\} = 0.4428 Q^2/Da \quad (5)$$

³ S. Levine and G. P. Dube (*in the Press*).

* The formula quoted in the earlier papers, namely

$(Q^2/2Da)/(1 + \ln 2) = Q^2/2Da/1.693$, is wrong.

and hence in the metallic case $f(2, 0)$ should be equal to 0.4428. It is found that $0.44 < f_2(2, 0) \leq 0.45$ by all three methods. As we now increase τ , a value of $\tau = \tau_0$ is reached such that $f_2(2, \tau_0) = f_1(2, \tau_0)$ and for $\tau > \tau_0$, $f_2(2, \tau) > f_1(2, \tau)$. However, according to the point method, the second approximation for the contact case again becomes equal to the first at $\tau \approx 6 > \tau_0$ and for $\tau > 6$, $f_2(2, \tau) < f_1(2, \tau)$ with the limiting value $f_2(2, \tau) \rightarrow -1/54\tau$ as $\tau \rightarrow \infty$. This is in sharp contrast to the limiting value $f_2(2, \tau) \rightarrow f_1(2, \tau) \rightarrow 1/16\tau^2$, obtained by the other two methods. The close agreement between the moment and the least square methods for $\tau < 5$ is to be noticed.

In order to understand why $f_2(2, \tau) > f_1(2, \tau)$ for large τ , we need only examine the behaviour of $f_r(2, \tau)$ and $f_a(2, \tau)$ separately. It is seen from Table VI that the first approximation to the repulsive term is greater than the second approximation (the difference being greatest for the point method). This is to be expected since the distortion of the charge distribution on each particle should be such as to lower the interaction energy. The same is true of the absolute value of the attractive term, i.e. $|f_a^{(2)}(2, \tau)| < |f_a^{(1)}(2, \tau)|$. The behaviour of $f_a^{(2)}(2, \tau)$ as a function of τ is similar to that of $f_a^{(1)}(2, \tau)$. We have already seen in I that there will be a diminution of (negative) charge density in the region between the two particles, when the distortion is introduced and hence a smaller attractive term. Further, the relative change in energy, as we pass from the first to the second approximation, is greater in the attractive term. Now for small τ , the positive term is much larger than the negative, $f_r(2, \tau) \gg |f_a(2, \tau)|$ and hence on the whole there is a lowering of energy when we pass from the first to the second approximation. However, for large τ , the two terms do not differ very much and the change in the attractive term is greater than that in the repulsive term leading to an increased resultant repulsion, i.e. $f_2(2, \tau) > f_1(2, \tau)$.

We next consider the variation of the energy function with distance as shown in Figs. 1, 2 and 3. This has been carried out for the moment method only since this is the simplest case to calculate and also the other two methods yield two quite similar curves. It is observed that at the minimum the second approximation lies above the first, i.e. $f_2(s_{\min.}, \tau) > f_1(s_{\min.}, \tau)$, and this remains true for all $s > s_{\min.}$. Now we have seen that the attractive term is larger (in magnitude) than the repulsive term at large distances (the ratio being proportional to the distance of separation). Similarly the correction to the attractive term is the more important at large distances and this tends to raise the potential curve. Also $f_r^{(2)}(s, \tau) < f_r^{(1)}(s, \tau)$ and $|f_a^{(2)}(s, \tau)| < |f_a^{(1)}(s, \tau)|$ for all s , and $f_r^{(2)}(s, \tau) \rightarrow f_r^{(1)}(s, \tau)$ and $f_a^{(2)}(s, \tau) \rightarrow f_a^{(1)}(s, \tau)$ (more slowly) as $s \rightarrow \infty$. Although $f_2(s, \tau) \rightarrow f_1(s, \tau)$ as $s \rightarrow \infty$ the difference between the two approximations does not diminish appreciably until $s > s_{\min.}$. Indeed, the greatest difference need not occur at contact, but at some value of $s > 2$. This is due to the slow approach of $f_a^{(2)}(s, \tau)$ to its asymptotic form $f_a^{(1)}(s, \tau)$. It should also be noticed that the minimum position $s_{\min.}$ for the second approximation is further out than that for the first.

We have seen that for the metallic particles, the moment and the least square methods give results which do not differ appreciably for $\tau < 5$. For insulating particles the determination of λ_1' is much more complicated than that in the metallic case. Hence we will only adopt the simplest method, namely the moment method, which should be reasonably satisfactory.

For the insulating particles, the value of λ_1' is positive, which was predicted in I. It is seen that as τ goes from 0 to infinity, λ_1' increases from zero to a maximum value, which is a function of the dielectric constant of the particle and then decreases to zero. For most insulating particles $\epsilon = D'/D$, the ratio of the dielectric constant of the particle to that of water, varies between 1/80 (gas bubbles) to 1/5. It is observed from the results in Table V that λ_1' does not change very much with ϵ .

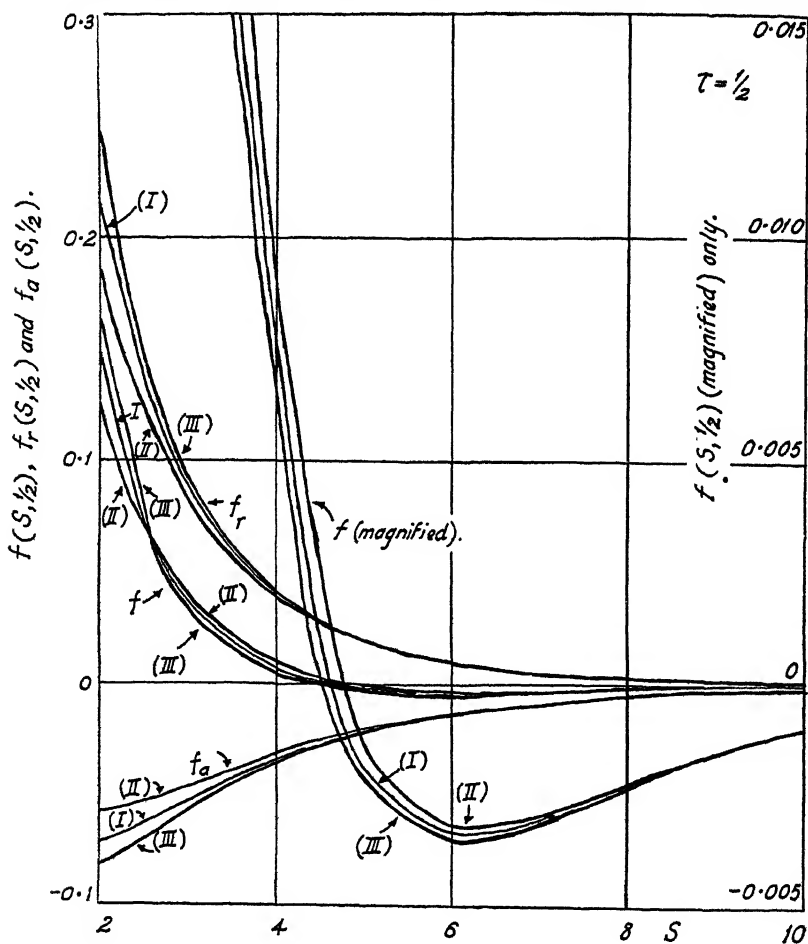


FIG. 1.

The same is true of the energy functions $f_r^{(2)}(2, \tau)$, $f_a^{(2)}(2, \tau)$ and $f_2(2, \tau)$ which have been evaluated for $\epsilon = 0.05, 0.10$ and 0.15 .

When $\tau = 0$, $f_1(2, 0) < f_2(2, 0)$ the difference being greatest when $\epsilon = 1/80$ while $f_1(2, 0) = f_2(2, 0) = \frac{1}{2}$ when $\epsilon = 1 (D' = D)$, as is to be expected. The behaviour of $f_2(2, \tau)$ in relation to $f_1(2, \tau)$ is exactly opposite to that in the metallic case, i.e., a value $\tau = \tau_0$ exists, such that $f_1(2, \tau_0) = f_2(2, \tau_0)$, with $f_1(2, \tau) < f_2(2, \tau)$ for $\tau < \tau_0$ and $f_1(2, \tau) > f_2(2, \tau)$ for $\tau > \tau_0$. As $\tau \rightarrow \infty$, $f_2(2, \tau) \rightarrow$, i.e. for large τ , the second approximation is practically independent of the dielectric constant of the particle.

Again the behaviour of the two terms in the energy $f_r^{(2)}(2, \tau)$ and $f_a^{(2)}(2, \tau)$ is similar to that of the corresponding terms for the first approximation.

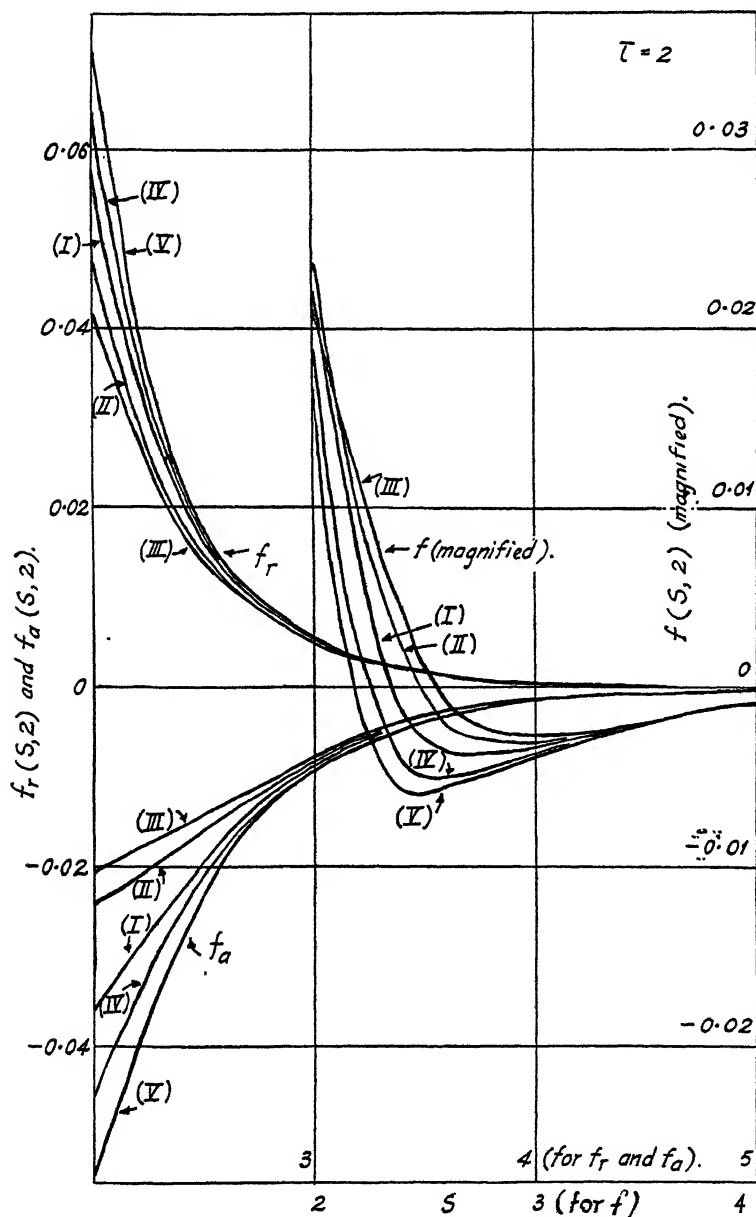


FIG. 2.

The difference from the metallic case is that $f_r^{(2)}(2, \tau) > f_r^{(1)}(2, \tau)$ and $|f_a^{(2)}(2, \tau)| > |f_a^{(1)}(2, \tau)|$ for all τ .

An explanation, similar to that given for the metallic case, is readily obtained for the behaviour of the second approximation at contact in

the insulating case. We need only recall that there will be an accumulation of negative charge in the region between the two particles as a result of the distortion and consequently an increase in the attractive term (in

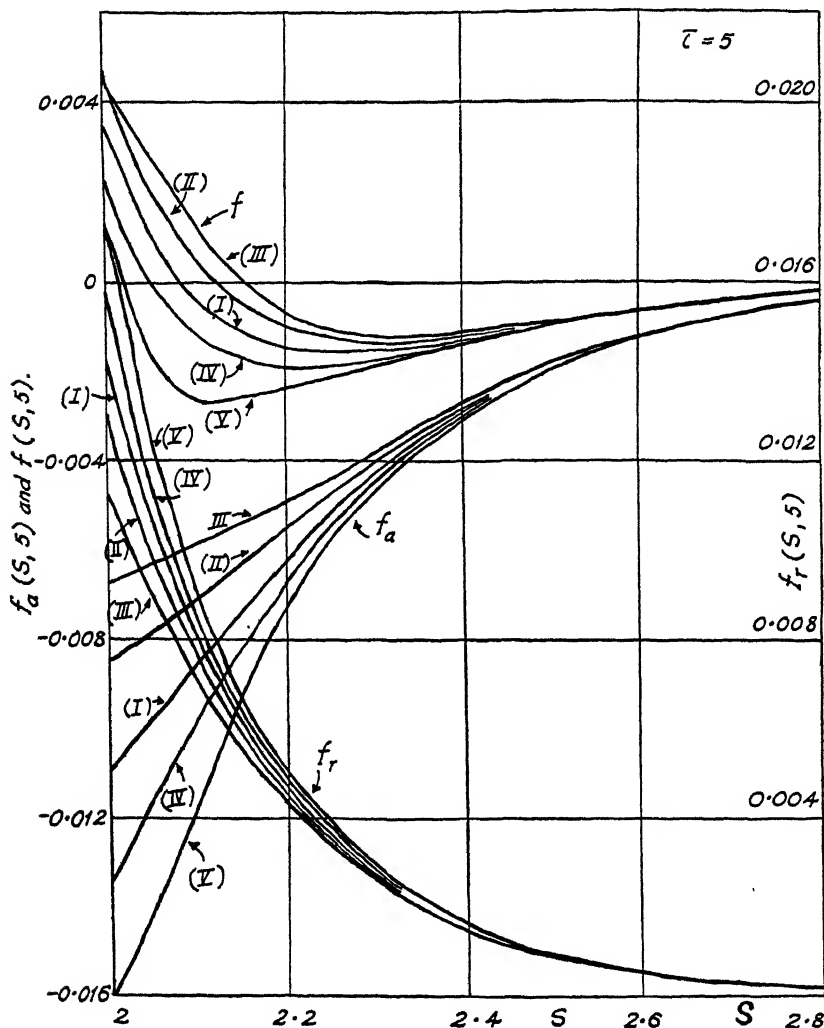


FIG. 3.

FIGS. 1, 2 and 3.—Variation of f 's (energy) with mutual separation(s). In each group of curves, denoted by f_r (repulsive) f_a (attractive) and $f = f_r + f_a$ (resultant); (I) first approximation, (II) second approximation, metallic case, (III) third approximation, metallic case, (IV) second approximation, insulating case, (V) third approximation, insulating case.

addition to that in the repulsive term). With this knowledge the argument proceeds along the same lines as in the metallic case.

The reason for the increase in the interaction energy at small τ , with the introduction of the polarisation terms, can be stated in a different way. The first approximation does not take into account the lower

dielectric constant inside the particles ($\epsilon < 1$) which would tend to increase the energy. This is only done with the second and higher approximations. When $\tau = 0$, we simply have two charged insulating spheres. To the best of our knowledge this case has not been worked out, although it would not be difficult to do so. The results of such an investigation would be some criterion towards indicating the rapidity of convergence of our method of approximation in the insulating case.

The energy was again plotted as a function of distance in Figs. 1, 2, 3. We need only remark that the second approximation now lies below the first in the vicinity of the minimum. In addition, the latter position has moved in towards smaller inter-particle distances.

4. Third Approximation.

We need not discuss the third approximation at the same length as for the second. In the metallic case, according to both the moment and least square method λ_1 and λ_2 show the same behaviour as λ_1' at contact, *i.e.*, they are negative except at $\tau = 0$ and ∞ where they are 0. Although $|\lambda_1| > |\lambda_2|$ for small τ ($\lambda_1 | \lambda_2 \sim \tau$), $\lambda_1 = \lambda_2$ at a certain τ , and for large τ , $|\lambda_1| < |\lambda_2|$ with a limiting ratio $\lambda_2 | \lambda_1 = 5/3$ as $\tau \rightarrow \infty$. According to the point method both λ_1 and λ_2 are also negative decreasing from 0 to $-3/11$ and $-2/11$ respectively as τ goes from 0 to ∞ . It is noticed that the difference between λ_1' and λ_1 is never very large.

When $\tau = 0$, there is very little difference between all three methods of determining λ_1 and λ_2 and hence in Table I, we have only given the values by the least square method. Furthermore, the second and the third approximations are practically the same. This implies that at least for small τ , the convergence of the series is rapid and the second approximation is sufficiently accurate. Unfortunately the same situation does not exist for all values of τ . No reliable method of estimating the rapidity of convergence has yet been found. An examination of Table VIII shows that only when τ becomes large, is there a considerable difference between the successive approximations. Perhaps the only safe conclusion that one can reach from this is that the first approximation is fairly satisfactory until we reach large values of τ ($\lesssim 10$). In the case of $\tau = 0$, the ratio of the first approximation to the true value is 1/0.89. Instead of finding a solution of the equation for the potential in terms of polar co-ordinates about each particle, it is more natural to choose bipolar co-ordinates. Unfortunately the equation is no longer separable in these co-ordinates except at $\kappa = 0$. However, it should be possible to apply a perturbation method for the limiting case $\tau \gg 1$.

The simplest and perhaps most instructive method of comparing the accuracy of the various types of approximations is to plot the variation of the potential over the surface of a single particle, when the particles are touching. The expression for the potential under consideration may be written as,

$$\psi^* = \tau e^\tau \psi / \kappa A = 1 + \frac{\tau}{u_2} e^{-(u_2 - \tau)} + \lambda_1 \left\{ \mu_1 \left(1 + \frac{1}{\tau} \right) + \mu_2 \left(1 + \frac{1}{u_2} \right) \frac{\tau}{u_2} e^{-(u_2 - \tau)} \right\} \\ + \frac{\lambda_2}{2} \left\{ (3\mu_1^2 - 1) \left(1 + \frac{3}{\tau} + \frac{3}{\tau_2} \right) + (3\mu_2^2 - 1) \left(1 + \frac{3}{u_2} + \frac{3}{u_2^2} \right) \frac{\tau}{u_2} e^{-(u_2 - \tau)} \right\}, \quad (6)$$

where $\mu_1 = \cos \theta_1$, $u_2 = \kappa r_2 = \tau \sqrt{5 - 4\mu_1}$ and

$$\mu_2 = \cos \theta_2 = (2 - \mu_1) / (5 - 4\mu_1)^{3/2}.$$

The quantity on the right-hand side has been plotted as a function of μ_1 for $\tau = 0.5, 2.0$ and 5.0 for the three different cases (Fig. 4, A, B and C). It is seen that there is a very little difference between the moment method and the method of least square deviation (the latter being the most satisfactory). We have also plotted (Fig. 4, E) the potential for the first, second and third approximations to show the rapidity of convergence for $\tau = 5$ (by the least square method).

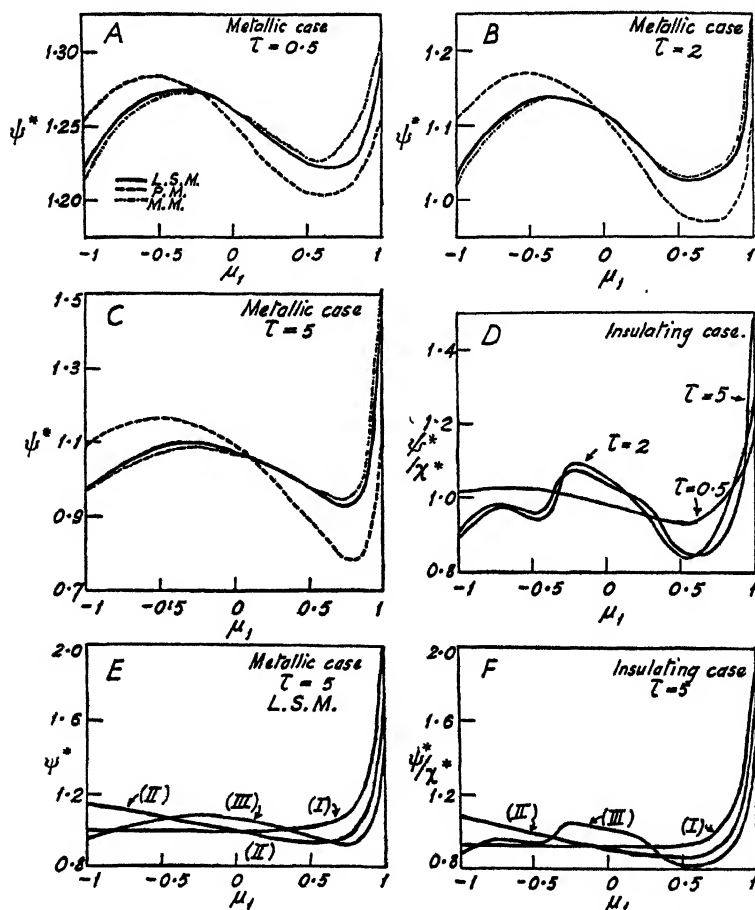


FIG. 4.—Variation of potential over surface of particles when in contact. In B and C, same legend as in A; in A, B, C and D, third approximation only; in D and E, (I) first ($\lambda_1 = \lambda_2 = B_1 = B_2 = 0$), (II) second ($\lambda_2 = B_2 = 0$) and (III) third approximation.

There is no marked difference between $f_3(2, \tau)$ and $f_2(2, \tau)$ for $\tau < 2$ and $f_3(2, \tau) > f_2(2, \tau)$ for large τ . We notice that the least square method and moment method give results which do not differ very much. Also the two terms $f_r^{(3)}(2, \tau)$ and $|f_a^{(3)}(2, \tau)|$ are both less than the corresponding quantities in the second approximation.

The energy functions $f_r^{(3)}(s, \tau)$, $f_a^{(3)}(s, \tau)$ and $f_3(s, \tau)$ have been plotted in Figs. 2 and 3 for the moment method. At the minimum

$$|f_3(s_{\min.}, \tau)| < |f_2(s_{\min.}, \tau)| < |f_1(s_{\min.}, \tau)|.$$

and this remains true for all $s > s_{\min.}$, with $f_3(s, \tau)$ tending towards $f_2(s, \tau)$ as $s \rightarrow \infty$. The energy expressions are not shown in Fig. 1 ($\tau = \frac{1}{2}$) because there is very little difference between the second and third approximation. The same is true in the insulating case.

For insulating particles, the behaviour of λ_1 and λ_2 is quite similar to that in the metallic case, the only difference being the change in sign. The only case that has been computed is $\epsilon = 0.10$. It is noticed that again there is not a considerable difference between the second and the third approximations for $\tau < 2$, but for larger τ the third approximation $f_3(2, \tau)$ becomes very much less. Also $f_r^{(3)}(2, \tau) > f_r^{(2)}(2, \tau)$ and $|f_a^{(3)}(2, \tau)| > |f_a^{(2)}(2, \tau)|$ for all τ . Finally we have again plotted the third approximation to the energy as a function of s . It is seen that, in the insulating case, $|f_3(s_{\min.}, \tau)| > |f_2(s_{\min.}, \tau)| > |f_1(s_{\min.}, \tau)|$. When $\tau = 5$, there is a considerable difference between $f_3(s, \tau)$ and $f_2(s, \tau)$.

The large deviation between the third and the second approximations at large τ is rather surprising, since it occurs to a much smaller degree in the metallic case. One would imagine that the polarisation effect is smaller for the insulating particles, but apparently this is not so for large τ . According to I (28) and (29), in the presence of a homogeneous field the ratio of the values of λ_1 in the insulating and the metallic cases is $(1 - \epsilon) \left(\frac{2 + 2\tau + \tau^2}{1 + \tau} + \epsilon \right)$. When $\tau = 0$, this ratio becomes $(1 - \epsilon)/(2 + \epsilon) < \frac{1}{2}$ and as $\tau \rightarrow \infty$ increases it steadily decreases, tending to $1/\tau$ as $\tau \rightarrow \infty$. However, this suggests a smaller polarisation effect for the insulating particles. An examination of the ratio of the potentials at the surface of each particle, ψ^*/χ^* where ψ^* is given by (6) and

$$\chi^* = B_0 + B_1 a \mu_1 + \frac{B_2}{2} (3\mu_1^2 - 1) \quad (7)$$

does not show a marked change from the second to the third approximation with respect to fluctuations from the true value $\psi^*/\chi^* = 1$ (Fig. 4F and also 4D). No satisfactory explanation of this deviation in the third approximation has yet been reached.

From these results one would at first have the impression that for $\tau > 3$ (*circa*), the first approximation is not satisfactory. However, the situation is more favourable than this for the following reasons. Firstly, no colloidal particle has a truly metallic surface. Secondly, it is doubtful whether the distribution of charge on the surface of the insulating particles remains uniform, as they approach. Assuming uniform distribution at large separation, it is more likely that there will be some displacement of charge, either by surface migration, desorption and re-adsorption or alignment of rotatable polar groups.* This displacement occurs to a maximum extent in the metallic case. We may, therefore, conclude that the purely metallic case is one limit and the insulating case with uniform distribution is the other limit. But the first approximation is roughly mid-way between the two limiting cases. Thus we believe that, when $\tau > 3$ the first approximation (in the insulating case) may be more satisfactory than one concludes from the results given here.

This situation is also suggested on examining the origin of the sign of λ_1 (or λ_2). The distortion of the ionic atmosphere corresponds to a positive contribution to λ_1 (or λ_2). The redistribution of charge on the

* The authors are indebted to Dr. F. Eirich for pointing this out.

(insulating) particle surface, however, leads to a negative contribution. The latter has been neglected above and hence the value of λ_1 (or λ_2) for insulating particles will probably be less than that calculated here, giving smaller corrections to the first approximation.

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Summary.

Numerical calculations have been carried out on the interaction energy of two colloidal particles, treating the cases described in the preceding paper. It is seen that for small particle radii or low electrolyte concentrations the first approximation is fairly accurate. For larger particles or more concentrated solutions of electrolyte the correction from the higher approximations may be quite considerable depending upon the amount of redistribution of charge on the surfaces of the interacting particles.

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KINETICS OF THE OXIDATION OF ORGANIC COMPOUNDS BY POTASSIUM PERMANGANATE. I. CYCLIC COMPOUNDS—2:6 DINITROPHENOL.

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Kinetic investigations of oxidation reactions involving KMnO_4 have been confined mainly to certain ionic reactions in which the oxidation was primarily brought about by an electronic transference from the ion oxidised to an intermediate manganese ion.^{1, 2, 3, 4} Hinshelwood^{5, 6} has studied the oxidation of certain cyclic organic compounds which ionise and concluded that these reactions were mainly bimolecular and were probably brought about by collision of the permanganate ion with the organic molecule. An induction period was

¹ Fales and Roller, *J.A.C.S.*, 1929, **51**, 345.

² Skrabal, *Z. anorg. Chemie.*, 1905, **42**, 1; Schilow, *Ber.*, 1903, **36**, 2735.

³ Launer, *J.A.C.S.*, 1932, **54**, 2597.

⁴ Launer and Yost, *ibid.*, 1934, **56**, 2571.

⁵ Hinshelwood, *J.C.S.*, 1919, 1180.

⁶ *Ibid.*, 1936, 368.

found with 2:6 dinitrophenol and he suggested that this was due, either to the repression of the quinonoid keto-form by the sulphuric acid, which was used up in the reaction, or to the inadequacy of the velocity of some reaction following the rupture of the benzene ring. The present work, however, shows that it is due to a slow process occurring during the reduction of the MnO_4' ion. This has been investigated, since Polissar⁷ has proved that all previous mechanisms for such reactions based upon an initial equilibrium of the type:



are invalid. New mechanisms have been proposed. These are applicable both to the oxidation of organic molecules and of anions and lead to a rate equation which is in good agreement with the experimental results.

Experimental.

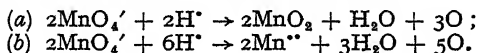
Materials.—Merck's dinitrophenol was crystallised several times from water and an aqueous solution (0.300 g. per litre) used throughout. The solution was stored in the dark since on long exposure to light, nitro-groups are reduced photochemically to amino-groups.⁸ Kahlbaum's KMnO_4 (M./50) and A.R. $\text{Na}_2\text{S}_2\text{O}_3$ (N./10) were standardised at frequent intervals. B.D.H. MnSO_4 contained 10.74 per cent. water.

Apparatus and Procedure.—The reaction was followed iodimetrically. Measured volumes of dinitrophenol and sulphuric acid were placed in a 500 c.c. flask, fitted with an electrical stirrer, and the KMnO_4 was contained in a separate vessel. Both were allowed to come to temperature equilibrium in a thermostat, electrically controlled at $30.02 \pm 0.02^\circ \text{C.}$, and then quickly mixed. The oxidation was arrested by the addition of N./2 KI (20 c.c.) and sufficient normal H_2SO_4 to maintain the total acid strength within the limits specified by Bray and Miller.⁹

Results.

No differences in rates were obtained using different rates of stirring, different cleansing agents, by "ageing" of the reaction vessel, nor when the reaction proceeded in the dark. The thiosulphate-iodine titration was accurate in presence of excess dinitrophenol, KI, KNO_3 and K_2SO_4 . Care, however, must be taken to avoid loss of iodine during titration. Separate determinations for each time interval were made since withdrawal of aliquot portions gave poor results due to the hydrated manganese dioxide formed adhering to the glass.

KMnO_4 may react according to equation (a) or (b),



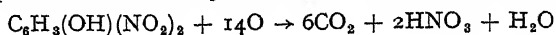
Excess KMnO_4 was allowed to react with dinitrophenol for 18 hours at 30°C. The amount of KMnO_4 used in oxidation, and the oxidising power of the precipitated MnO_2 , both expressed in terms of the iodine liberated, were determined separately by the addition of acidified KI. The ratios of the two iodine values were 1.496, 1.506, and 1.514, for acid normalities of 0.000165, 0.00154 and 0.0615 respectively, as compared with 1.5, the theoretical value if equation (a) is wholly obeyed. Above 0.0615 N. acid, KMnO_4 reacts partly in the manner of equation (b).

⁷ Polissar, *J.A.C.S.*, 1936, 58, 1372.

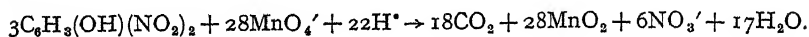
⁸ Molnar, *Compt. rend.*, 1935, 201, 1482.

⁹ Bray and Miller, *J.A.C.S.*, 1924, 46, 2204.

Dinitrophenol is oxidised by KMnO_4 according to the equation :



or,



50 c.c. dinitrophenol was allowed to react with excess KMnO_4 and H_2SO_4 for 5 days at 30°C . Blanks, without dinitrophenol, were performed simultaneously, since KMnO_4 deteriorates under these conditions. The loss of oxidising power in terms of N./10 iodine, correcting for deterioration, was an average of 22.84 c.c. compared with the theoretical value of 22.80 c.c.

Rate Determinations : (Temp. 30.02°C).

Series A.—Total acid normality from 0.000615 to 0.308; 50 c.c. each of KMnO_4 and dinitrophenol; total volume of 170 c.c. Fig. 1 gives the

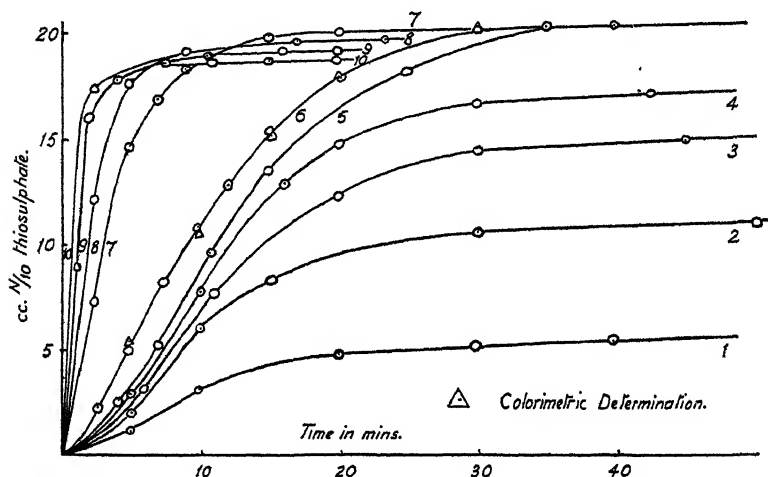


FIG. 1.

Curve No.	Total Sulphuric Acid Normality.
1	0.00
2	0.000615
3	0.00123
4	0.00154
5	0.00246
6	0.0123
7	0.0615
8	0.123
9	0.246
10	0.308

plot of loss of oxidising power of KMnO_4 (as c.c. N./10 $\text{Na}_2\text{S}_2\text{O}_3$) against time in mins. An induction period is evident except at high acidity. The decrease in the end point of the curves 8, 9, 10 is due to the KMnO_4 partly acting as in equation (b). The rate of oxidation, obtained by the tangent method, increased rapidly at first to a sharp maximum and then decreased according to a second order equation.

The pH was determined throughout the reaction, since in the acid normalities used, the dinitrophenol exists both as ions and molecules, and since acid is consumed during the oxidation. A glass electrode was used in conjunction with a Cambridge electrometric valve pH meter and 10 c.c. solution were transferred to the electrode at definite times. The

instrument was calibrated at intervals against a standard B.D.H. phthalate buffer solution. From the H^+ concentration at the point of maximum velocity, the concentration of unionised dinitrophenol was found, assuming that its pK value¹⁸ was 3.62, and that it obeyed the "common-ion law." This concentration was approximately proportional to the maximum velocity, showing that the dinitrophenol molecule was the reacting species. In Fig. 2 the plot of $M/\text{maximum velocity}$ is plotted against M , where M is the concentration of the dinitrophenol molecules. This is discussed later.

Quantitative experiments show that the loss of oxidising power of the $KMnO_4$ is the same as the amount of dinitrophenol oxidised. Curve 6, Series A, has been repeated by arresting the reaction at definite times by 20 c.c. acidified KI and removing the iodine by thiosulphate. To this, 5 g.

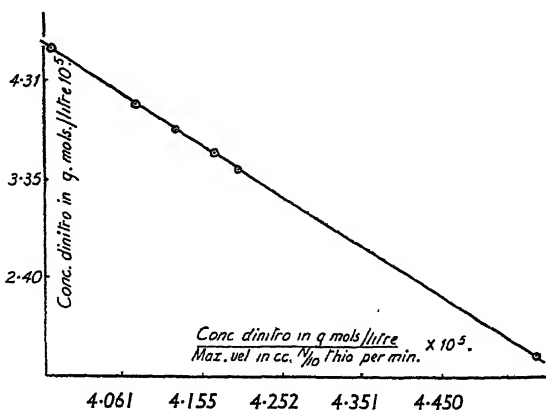


FIG. 2.

of sodium acetate were added to buffer it. In a separate vessel, 50 c.c. $KMnO_4$ were decolorised by 20 c.c. acidified KI, and titrated with thiosulphate, and to this was added 5 g. of sodium acetate and approximately the same amount of dinitrophenol as should have been unoxidised in the experiment above. These two solutions of the same pH and containing equal amounts of all electrolytes were compared colorimetrically by a Kober colorimeter. The amount of unoxidised dinitrophenol at any time is thus found and is incorporated in Fig. 1; the agreement is good.

Series B.—Vol. of dinitrophenol from 25 c.c. to 100 c.c.; 50 c.c. of $KMnO_4$, acid normality of 0.00246; total volume of 170 c.c. The results are given in Table I. The plot of $(M)/\text{maximum velocity}$ against (M) is again a straight line.

TABLE I.

Time in Mins.		C.c. of N/10 Thiosulphate.					
2.5	.	0.50	1.04	1.56	1.70	1.97	2.78
5	.	1.31	2.27	3.50	3.63	4.60	6.24
10	.	3.25	5.24	7.91	8.42	11.75	14.38
15	.	5.63	8.00	12.53	15.34	17.14	21.29
20	.	7.70	12.19	15.99	19.00	21.64	24.82
30	.	9.70	15.27	19.50	22.64	24.80	27.64
40	.	10.48	15.91	20.74	24.08	25.80	28.51
60	.	10.78	16.34	21.10	24.41	26.41	29.06
Vol. c.c. dinitro.	.	25	37.5	50	62.5	75	100

Series C.—Vol. of $KMnO_4$ from 25 to 75 c.c.; 50 c.c. dinitrophenol; acid normality of 0.00246; total volume of 170 c.c. Table II summarises the results. After the point of maximum velocity, all curves in the three

¹⁸ Clarke, *Determination of Hydrogen Ions*, 1928.

TABLE II.

Time in Mins.	C.c. of N/10 Thiosulphate.					
2.5	0.85	1.02	1.21	1.46	1.56	1.86
5	1.88	2.30	2.70	3.22	3.50	4.01
10	4.77	5.50	6.76	7.42	7.91	9.00
15	8.05	9.01	10.80	11.61	12.52	13.96
20	10.90	12.16	14.04	14.90	15.99	17.38
30	13.98	16.30	17.88	18.58	19.50	20.58
40	15.03	17.68	19.73	20.20	20.74	21.24
60	16.00	18.53	20.81	21.08	21.10	21.49
Vol. KMnO_4 in c.c. .	25	30	37.5	42.5	50	75

series give good second order plots except (a) near the end of the reaction (where complex formation begins), (b) at high concentrations of KMnO_4 (when it becomes pseudo-monomolecular), and (c) at high concentrations of dinitrophenol (when it retards the reaction). The plot of the maximum velocity against concentration of KMnO_4 at this point is a straight line.

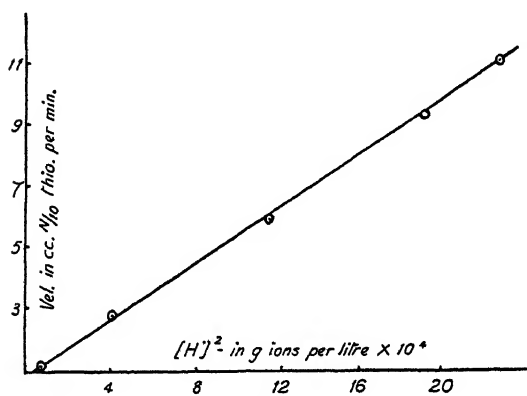


FIG. 3.

be negligible here. Complex anion formation between Mn^{+++} ions and dinitrophenol has been detected to a very small extent near the end of the reaction. There is no complex formation between dinitrophenol and MnO_2 .¹¹

Addition of Hydrated MnO_2 , KF and MnSO_4 .

Freshly precipitated MnO_2 caused an acceleration when the total acidity exceeded 0.0615 but had no effect below this normality. Since all the dinitrophenol is present in the unionised form, this is probably due to the dissolution of the dioxide and the consequent production of Mn^{+++} ions. Fig. 3 gives the plot of the initial velocity against the square of the H^+ ion concentration in acidities greater than 0.0615 N.

Complex Formation and Neutral Salt Effect.

Large concentrations of both KNO_3 and K_2SO_4 had no measurable effect on the rates, but magnesium sulphate caused a slight rise.* The effect is so small as to

TABLE III.

Initial Rate in C.c. N/10 $\text{Na}_2\text{S}_2\text{O}_5$ per Min.	Conc. MnSO_4 in g. Anhydr. MnSO_4 per Litre.
1.47	0.1578
1.95	0.3156
2.61	0.4734
3.15	0.6312
3.15	0.7890
3.15	0.9880
3.15	1.5780

* Cf. ¹², ¹³, and ².¹¹ Bernardi, *Gazz. Chim. Ital.*, 1930, 60, 169.

Fluorine ions form a stable complex ion with Mn^{+++} ion (MnF_4^-). Addition of KF therefore retards the rate of oxidation and in large concentrations the reaction is almost completely inhibited.

The addition of $MnSO_4$ accelerates the initial rate of oxidation.

Table III summarises the results using 50 c.c. each of $KMnO_4$ and dinitrophenol, an acid normality of 0.0123 and a total volume of 170 c.c. at 30° C. The rate at first increases linearly with concentration of $MnSO_4$, but then slows down and reaches a maximum velocity over the range of concentration used — above 1.578 g. $MnSO_4$ per litre, the rates were too difficult to measure idiometrically. At this concentration, there is no induction period and the reaction is kinetically of the second order.

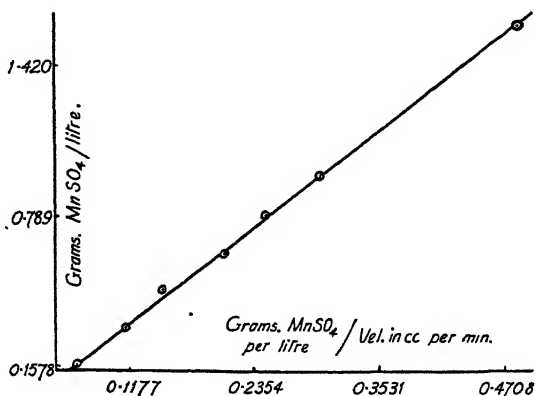


FIG. 4.

Fig. 4 is the plot of $(MnSO_4)/\text{initial velocity against } (MnSO_4)$ showing that the initial rate is proportional to the function $(MnSO_4)/(k_1 + k_2(MnSO_4))$, where k_1 and k_2 are constants.

Heats of Activation.

Series D.—Vols. of dinitrophenol from 15 to 50 c.c.; acid normality of 0.0123; 50 c.c. of $KMnO_4$ and total volume of 170 c.c., together with

TABLE IV.

Time in Mins.	C.c. N/10 Na ₂ S ₂ O ₃ .				Time in Mins.	C.c. N/10 Na ₂ S ₂ O ₃ .			
Temperature, 35.00° C.					Temperature, 30.02 °C.				
1	7.78	6.56	5.89	4.51	1	5.26	4.32	3.49	2.81
2	10.92	9.72	8.42	5.99	2	8.98	—	6.29	5.99
3.5	11.92	11.16	9.48	6.31	2.5	—	8.54	—	5.14
5	12.32	11.62	9.92	6.48	3.5	11.62	—	8.28	—
					5	12.22	10.75	9.00	5.70
					7.5	12.32	11.10	9.50	6.03
Temperature, 25.01 °C.					Temperature, 20.00 °C.				
1	3.02	2.70	2.20	1.60	1	1.57	1.20	0.90	0.60
2.5	7.87	6.60	5.63	4.08	2.5	5.48	4.40	3.66	2.20
5	10.88	9.48	7.98	5.40	5	8.84	7.50	6.22	4.52
7.5	11.10	9.82	8.30	5.76	7.5	10.40	8.98	7.22	5.20
Vol. c.c. dinitro.	50	35	25	15		50	35	25	15

25 c.c. of $MnSO_4$ solution (6.871 g. per litre), at temperatures of 20.00, 25.01, 30.02, 35.00 and 40.00° C. These are collected together in Table IV. Good bimolecular constants are obtained but these vary with the concentration of the dinitrophenol, but the plots of log. (velocity constants

in g. mols. per litre per min.) against $1/T$ gives a series of straight lines, all of which have the same slope (Fig. 5). The heat of activation calculated from the slope is 14,400 cal.

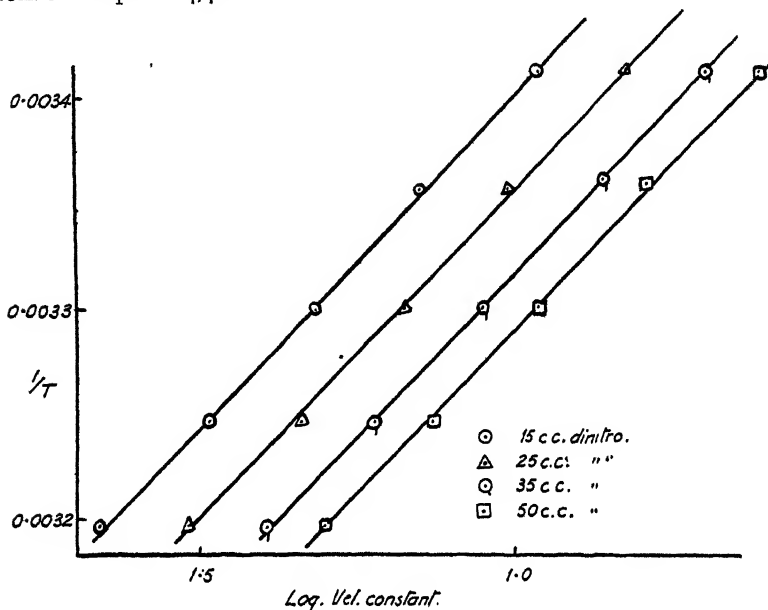


FIG 5

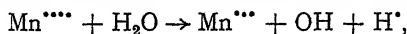
Discussion.

The oxidation of 2 : 6 dinitrophenol in presence of sufficient MnSO_4 is similar to that of picric acid¹² and other nitrated phenols⁵ in being best represented kinetically by a second order equation. This, however, is not due to a reaction brought about by collisions of MnO_4' and the dinitrophenol molecule, because Mn^{+++} accelerates the oxidation by producing higher concentrations of Mn^{+++} ions and thereby causing a decrease in the MnO_4' ion concentration. Furthermore, large concentrations of KF almost inhibit the reaction by reducing the concentration of intermediate Mn ions, thus showing that the MnO_4' ion itself performs little or no oxidation work. The potency of Mn^{+++} and Mn^{++++} ions in oxidation as measured by their normal oxidation potentials is only slightly greater than that of the MnO_4' ion, but they are more effective because they may oxidise by an electronic transference and the heat of activation will equal the heat of solution together with small heat changes caused by the different hydration of the ions involved, whereas the reduction of MnO_4' involves the rupture of four covalency bonds and thus is associated with a high activation energy, and also, it will be a reaction of high complexity involving rate equations of high and improbable order. Launer³ has shown with oxalic acid that Mn^{++++} ions are more effective in oxidation than are Mn^{+++} ions and similar experiments with KF and with MnSO_4 (to be discussed later) in the oxidation of dinitrophenol suggest the same conclusion. The oxidation

¹² Moelwyn-Hughes, *Trans. Faraday Soc.*, 1933, **29**, 1162.

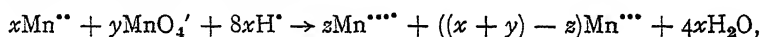
¹³ Redmon, *J.A.C.S.*, 1935, **57**, 2246.

here, however, cannot proceed simply by an electronic transference to the Mn^{***} ion, since a large number of oxygen atoms are added to the molecule. We suggest that Mn^{***} ions react with water:

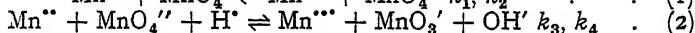
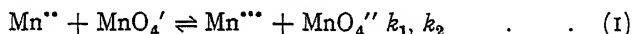


thereby producing OH radicles, which will be highly reactive and still possess the abnormally high mobility of the hydroxyl ion.¹⁴ These radicles on collision with the dinitrophenol molecule form an addition compound, which either breaks down rapidly, or first adds on a further OH radicle, and then a ring rupture, with formation of straight chain unsaturated aliphatic compounds, follows. An intermediate oxidation compound of dinitrophenol has been prepared which is oxidised *much more rapidly* than is dinitrophenol.

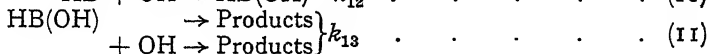
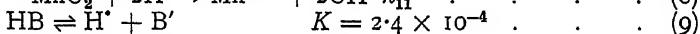
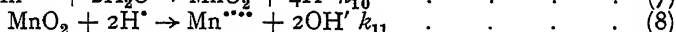
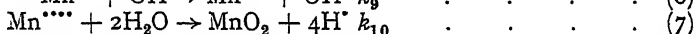
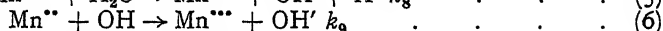
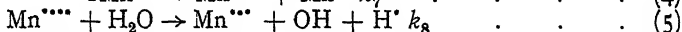
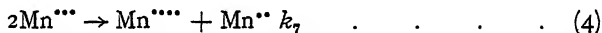
The actual mechanism of the production of intermediate ions by the interaction of Mn^{**} and MnO_4' ions has always been left open and equilibria of the general type:



i.e., a sum of a series of rapid equilibria, have been proposed. Such equilibria, according to Polissar⁷ cannot exist. The following are therefore proposed and these allow an equilibrium between Mn^{**} and MnO_4' ions to take place without disagreeing with his experimental results.



These equilibria account for the production of Mn^{***} as the first identifiable stage in all oxidations by KMnO_4 and also for the greater stability of KMnO_4 in alkaline solutions. In oxidation reactions, these are followed by



Equations 4, 5, 6, together, are the equilibrium $2\text{Mn}^{***} \rightleftharpoons \text{Mn}^{****} + \text{Mn}^{**}$; Mn^{***} ions may either produce OH radicles (eqn. 5) or be hydrolysed to MnO_2 (eqn. 7); eqn. 8 is probably a composite reaction, but further sub-division does not change the conclusions deduced below; eqn. 9 represents the dissociation of dinitrophenol, where HB is the undissociated molecule. The solution of these reactions is based on the assumptions that equations 1, 2 and 3 are sensibly irreversible in oxidation and that k_{13} is greater than k_{12} , and is:

Rate of oxidation:

$$\frac{k_{12}(\text{H}^{\cdot}/(\text{H}^{\cdot} + \text{K})) \cdot D \cdot (3k_9k_1(\text{Mn}^{**})(\text{MnO}_4') + k_{11}k_8(\text{MnO}_2)(\text{H}^{\cdot})^2)}{k_9(k_{10} - k_8)(\text{Mn}^{**}) + k_{10}k_{12}D(\text{H}^{\cdot}/(\text{H}^{\cdot} + \text{K}))},$$

¹⁴ Ubbelohde, *J.C.S.*, 1935, 1605.

where D is the *total* concentration of dinitrophenol, and $(H^+)/(H^+ + K)$ is the factor to convert this to a concentration of unionised molecules.

At low H^+ concentrations, $k_{11}k_8(MnO_2)(H^+)^2$ is negligible, since (MnO_2) is the concentration of MnO_2 in *solution*, and is thus very small. Hence the rate is roughly proportional to the concentration of unionised dinitrophenol molecules, or more exactly, to the function

$$(HB)/(K_1(HB) + K_2)$$

(where K_1 and K_2 are constants, if all concentrations, except that of H^+ ion, are constant), as has been shown in Fig. 2. Higher concentrations of dinitrophenol thus cause a retardation as has been found experimentally. At high H^+ concentrations, $(H^+)/(H^+ + K)$ is unity, since K is small, but the term $k_{11}k_8(MnO_2)(H^+)^2$ is now important and the rate varies as the square of the H^+ concentration in high acidities (Fig. 3). This further accounts for the catalytic effect of MnO_2 in strong acid solutions and for the fact that $KMnO_4$ partly reacts according to equation (b) in acid normalities greater than 0.0615.

The addition of $MnSO_4$ in small amounts accelerates the rate in direct proportion to its concentration because $k_9(k_{10} - k_8)(Mn^{IV})$ is small compared with $k_{10}k_{12}D(H^+)/(H^+ + K)$, but in higher $MnSO_4$ concentrations, the first term becomes increasingly important and should finally retard the reaction. The retardation has been found by Launer³ in the oxidation of oxalic acid, and also in the present work using the gasometric method employed by him. This inhibitory effect is caused by the removal of OH radicals by Mn^{IV} (eqn. 6); and the term $(k_{10} - k_8)$ is a measure of the relative amount of Mn^{IV} ion producing OH radicals to that removed by hydrolysis (eqns. 5 and 7 respectively). When all concentrations, except that of $MnSO_4$ are constant, the theoretical equation reduces to the form $(MnSO_4)/((k_1 + k_2)(MnSO_4))$ as found experimentally (Fig. 4). The twofold effect of $MnSO_4$ may be regarded as evidence that Mn^{IV} ions lead to the production of OH radicals, and not as Ubbelohde¹⁴ suggested, by Mn^{III} reacting with hydroxyl ions, $Mn^{III} + OH^{\cdot} \rightarrow Mn^{IV} + OH$, because this latter mechanism would account for the initial acceleration but not for the retardation at higher concentrations. It must be emphasised that in all work in which high Mn^{III} concentrations have been assumed, the conditions used favoured complex formation and these complex anions dissociate only to a very small extent.^{1, 15} The theoretical equation in addition shows that the rate is first order with regard to $KMnO_4$.

The heat of activation of 14,400 cal. is 8% less than that found by Hinshelwood (15,600 cal.). The lower value is probably the more accurate because, in his work, an induction period was still present at the three lower temperatures, in acidities which were never greater than 0.01 N. (cp. curve 6, Fig. 1 here), and the equation used in calculating the velocity constants was not well obeyed by 2:6 dinitrophenol. In consequence, the plot of $\log(\text{velocity constant})/1/T$ did not give a straight line of well-defined slope. The agreement, however, is satisfactory and means that the addition of $MnSO_4$ merely allows a greater production of intermediate Mn ions without altering the mechanism and we must therefore assume (with all other workers) that there is always present a minute concentration of Mn^{IV} ions in "pure" $KMnO_4$ solution. Hinshelwood found that the heat of activation varies with

the structure of the dinitrophenols and related compounds, and thus showed that the heat measured does not relate to any process in the reduction of the MnO_4' .

The complete equation is: $v = P \times 2.29 \times 10^{11} e^{-14,400/RT}$, where P has the order of unity and varies with the concentration of the dinitrophenol. This variation is probably due to steric factors since the molecule is complex and polar, or to a small amount of association at higher concentrations.

The mechanism in which OH radicles play a predominant rôle may explain the course of the reaction of KMnO_4 with unsaturated aliphatic compounds, where 2OH radicles are added to two adjacent carbon atoms, *e.g.*, C_2H_4 to glycol, and also the appearance of small quantities of H_2O_2 in the oxidation of oxalic acid in presence of gaseous oxygen, which acts as a deactivator in three-body collisions.¹⁶ Further work is continuing with dinitrophenol and the two suggestions above are being examined.

Summary.

The oxidation of 2 : 6 dinitrophenol by KMnO_4 in aqueous solutions of low acidity has been studied kinetically. The reaction is complex and has an induction period due to the slow reduction of MnO_4' to Mn^{+++} ions. The latter reacts with water producing OH radicles which are responsible for the oxidation. The mechanism proposed agrees well with the experimental conclusions and is applicable to the oxidation of organic anions and neutral molecules. The heat of activation associated with the oxidation is 14,400 cal.

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¹⁶ Launer, *J.A.C.S.*, 1933, 55, 865.

THE ADSORPTION OF THE HYDROUS METALLIC OXIDES BY KIESELGUHR.

BY E. C. C. BALY, W. P. PEPPER and C. E. VERNON.

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The adsorption of alumina by kieselguhr was described in a preliminary note¹ and more recently the adsorption of other hydrous oxides has been investigated. The kieselguhr used was the "Superfloss" brand of the Johns-Manville Company and it is important to note that the quantities of the hydrous oxides which completely coat 100 g. of kieselguhr refer to this product only.

It was necessary at the outset to obtain an approximate value of the surface area of 100 g. of the kieselguhr in order to correlate this with the nature of the adsorbate. Two series of measurements of the rates of sedimentation of the particles in aqueous suspension were made by the International pipette method, it being assumed that the particles

¹ E. C. C. Baly and W. P. Pepper, *Nature*, 1935, 136, 28.

were spherical. From these measurements the W , $\log r$ or cumulative percentage curve was drawn, where W is the percentage weight of the particles having radius equal to or greater than r . By differentiation of this curve the values of $dW/d \log r$ were obtained and from these the values of $dS/d \log r$ were calculated, where S is the surface area. The $dS/d \log r$, $\log r$ curve was then drawn and the area under this curve gave the total surface area of 100 g. of the kieselguhr. The two series of measurements gave values which agreed within the limits of experimental error and the mean value was 1.54×10^6 sq. cm. Although this value is less than the true effective surface area, it is of some importance in that it may be accepted as a specification of the kieselguhr.

It was found that the "Superfloss" kieselguhr contained small amounts of clay and organic matter and it was necessary to remove these impurities before measurements of its adsorptive power were made. The clay and part of the organic matter were removed by repeated extraction with hydrochloric acid, the last traces of organic matter being oxidised by heating the extracted kieselguhr at 600° in a current of air.

About 5 kg. of the kieselguhr were heated for 5 hours with 15 l. of 4 N. HCl in an enamelled iron dish, the dark oily matter which separated being removed by means of filter paper. Fresh acid was added from time to time to make good the loss by evaporation. The kieselguhr was collected about one-third at a time by suction on an 11 in. Buchner funnel and washed with boiling distilled water until the filtrate was colourless. Since the kieselguhr on the funnel, when no further water can be abstracted by suction, still contains sufficient to cause it to flow when removed from the funnel, it was necessary to disconnect the filter flask from the pump and gently to tap the bed of kieselguhr all over the surface with a large flat glass stopper. This caused the particles to form a more compact mass with the result that the whole become semi-fluid. The separated water was then removed by suction and the process was repeated until no more water could be extracted.

The kieselguhr was again extracted, about 300 g. at a time, with boiling 4 N. HCl, this being repeated until the acid extract gave no reaction for ferric iron with NH_4CNS . The extracted kieselguhr was then washed until it was completely free from acid and the following procedure was found to be essential. The kieselguhr after being washed on the funnel with 10 litres of distilled water was then divided into two approximately equal portions. One portion at a time was completely disintegrated by vigorous stirring in 7 l. of distilled water and steam at 15 lb. pressure was blown in until the suspension boiled, after which it was filtered immediately. Owing to the fact that the kieselguhr contained particles with widely different sedimentation rates it was essential to stir the suspension continuously and to transfer it to the funnel by means of a ladle. This washing process was repeated until the filtrate was neutral to B.D.H. indicator and when this end had been achieved the kieselguhr was dried overnight at 125° .

Before heating the kieselguhr in air at 600° it was necessary to disintegrate it. This disintegration presented a problem of some difficulty because when small lumps of it were crushed on glazed paper by a spatula small coherent laminæ were formed which materially decreased the effective surface area. The only satisfactory method of disintegration was to shake the small lumps in a tin-plate tube 30 in. long and 3 in. wide which was provided with a tightly fitting lid at each end.

The finely disintegrated material was heated in a transparent vitreosil tube, care being taken that more than two-thirds of the diameter of the

tube were not filled. The tube and its contents were heated at 600° in an electric resistance furnace for 8 hours, a current of dry filtered air being passed continuously through it. At frequent intervals the tube was slowly rotated through several revolutions.

The purified kieselguhr was remarkably constant in its properties. A great number of batches prepared during the course of this investigation showed no variation whatever in adsorptive power, and the effective surface area of 100 g. was found to be 2.869×10^6 sq. cm. as will be explained later.

In the early stages of the investigation considerable difficulties were experienced owing to the remarkable power of adsorbing water and OH ions possessed by the hydrous oxides which causes their flocculation before they have been adsorbed by the kieselguhr. As an example of this it was stated in the preliminary communication that ferric hydroxide is not adsorbed by kieselguhr. It was found later that this was due to flocculation of the ferric hydroxide taking place as the result of the concentration being too great, the flocculated material not being adsorbed.

As the result of investigation it was quantitatively proved that when the purified kieselguhr is suspended in a very dilute solution of either ferric or thorium nitrate, in which the salt is very largely hydrolysed, adsorption of the oxide takes place until an equilibrium state is established between the amount adsorbed and the amount remaining in solution. This equilibrium is progressively shifted towards the adsorbed state by the slow addition of a very dilute solution of ammonia until the whole of the oxide has been adsorbed. On this fact was based the method whereby the adsorptive power of the kieselguhr towards each of these two oxides was determined.

In each determination 10 g. of the purified kieselguhr were de-flocculated in 100 ml. of water by means of a serrated disc electrically driven at 1500 revs. per minute. The de-flocculated suspension was de-aerated by warming under reduced pressure and then added to a vigorously stirred solution of a known amount of the nitrate in 1 l. of water in a 2 l. beaker. The stirrer, which had blades $1\frac{1}{4}$ in. long and was electrically driven at 250 revs. per minute, was placed close to the side of the beaker in order to avoid the formation of a central vortex in the suspension.

An equivalent quantity of ammonia in 500 ml. was then added very slowly to the suspension by means of the 250 ml. burette shown in Fig. 1. The object of the bulb and jet just below the stopcock was to enable the rate of flow of the alkali to be observed and controlled at about 5 drops a second. The burette was held in position so that the end of the capillary delivery tube was immediately above the blades of the stirrer. After the whole of the ammonia solution had been added, the coated kieselguhr was collected on a 4-in. Buchner funnel, washed with 1 l. of water and dried overnight at 60°. A series of preparations were made by this method, using progressively larger amounts of the nitrate until the adsorptive power of 10 g. of the kieselguhr had been exceeded.

The foregoing method was not found to be necessary in the case of alumina and in this case the maximum concentration of the nitrate solution was 0.007 M. with respect to Al_2O_3 , and the ammonia in more concentrated solution was added in slight excess.

In order to examine the effect of the adsorbed layer of metallic oxide, the surface potential of each preparation was determined by the method of cataphoresis. Some difficulty was experienced with aqueous sus-

pensions owing to the surface potential in many cases being insufficient to prevent flocculation. Much more stable suspensions were obtained in 0.0524 N. acetic acid with pH 29.8, prepared by diluting 15 ml. of the pure glacial acid to 5 l. It is of interest to note that the ζ -potentials of both electronegative and electropositive powders are enhanced when in suspension in this acid. Thus the ζ -potential of pure kieselguhr is increased from -0.035 volt in water to -0.050 volt in 0.0524 N. acetic acid, whilst those of the electropositive preparations are also enhanced in this acid.

In every case a suspension of 0.5 g. in 100 ml. of the acid was used

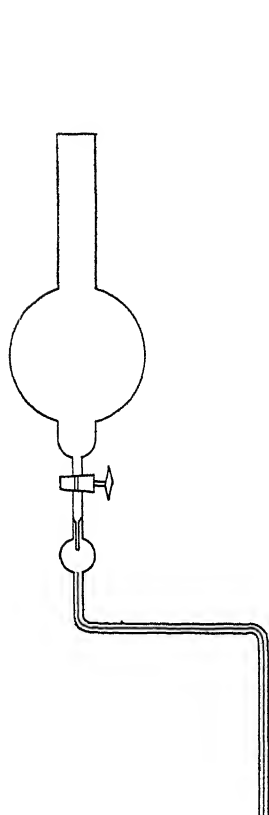


FIG. 1.

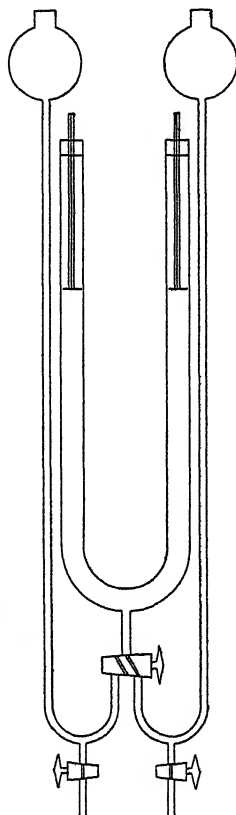


FIG. 2.

and it was proved that at room temperature the adsorbed oxide is not acted on by the acid. The modified form of Burton tube shown in Fig. 2 was used and found to be exceedingly convenient, one bulb being used for the suspension and the other for the 0.0524 N. acetic acid. A potential difference of 220-230 volts was applied for 5 minutes, and during this period the temperature rose about 1° , the mean temperature being adopted. We are indebted to Mr. H. Rogan for determining the dielectric constant of the acid and his value of 79.41 was used in calculating the ζ -potential, the viscosity being assumed to be the same as that of water.

The curve A in Fig. 3 shows the relation between the ζ -potential and the amount of alumina adsorbed and indicates that 100 g. of kieselguhr are completely coated by 0.00243 g. mol. of Al_2O_3 , a maximum ζ -potential of $+0.0754$ volt being then obtained. The first portion of the curve which is linear indicates that the kieselguhr progressively adsorbs the same molecular units until it is completely coated with a single layer of those units. Assuming the symmetrical distribution of the molecular units on the surface, the diameter of each unit will be the square root of the area covered by two units. If these units are molecules of Al_2O_3 the number of groups of two molecules adsorbed on 2.86893×10^6 sq. cm. is $0.00243 \times 3.03 \times 10^{23}$.

The diameter of each molecule is found to be 6.242×10^{-8} cm. and this is the same order of magnitude as that given by X-ray measurements of crystalline Al_2O_3 . Assuming that the units adsorbed are $\text{Al}(\text{OH})_3$ molecules the molecular diameter is found to be 4.414×10^{-8} cm. and this is smaller than that of crystalline $\text{Al}(\text{OH})_3$. It may be concluded, therefore, that the kieselguhr adsorbs a unimolecular layer of Al_2O_3 .

The second portion of curve A in Fig. 3 expresses the ζ -potential of mixtures of the completely coated kieselguhr with increasing quantities of free alumina. As would be expected the ζ -potential decreases until it becomes constant at $+0.0612$ volt which is that of free alumina. The most striking fact revealed by this curve is the enhancement of the ζ -potential of alumina from $+0.0612$ volt to $+0.0754$ volt when it is adsorbed as a uni-molecular layer. This enhancement is not peculiar to alumina, since it has been proved to be characteristic of every

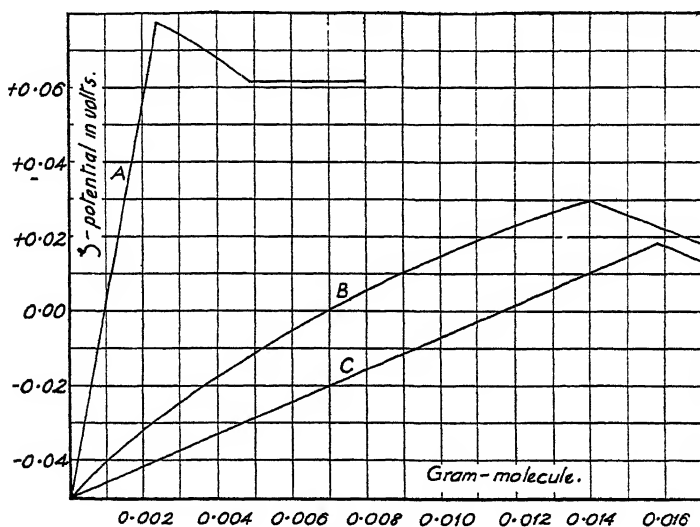


FIG. 3.

A U_2O_5 .B NiO containing ThO_2 in the molecular ratio of $1\text{ThO}_2 : 29 \text{ NiO}$.C CoO .

substance, whatever may be the molecular units adsorbed. The phenomenon indicates that adsorption complexes are formed in which the molecular units of the adsorbates are activated. The formation of adsorption complexes and the activation of the adsorbate in the adsorption of gases on solid surfaces has been discussed in a previous communication.²

The adsorption of thorium oxide by kieselguhr is also restricted to a single uni-molecular layer and 100 g. are completely coated by 0.0028939 g. mol. of ThO_2 , the maximum ζ -potential being $+0.038$ volt. The diameter of the ThO_2 molecule calculated from this is 5.72×10^{-8} cm. and this is only a little greater than 5.59×10^{-8} cm. which is the molecular diameter in the crystalline oxide.

The investigation of the adsorption of the oxides of cobalt and nickel

² E. C. C. Baly, *Proc. Roy. Soc., A*, 1937, 160, 465.

by kieselguhr presented a problem of considerable interest. In the first place the nitrates of these metals are not hydrolysed to any measurable extent in aqueous solution even at very great dilution, and consequently no adsorption takes place on the addition of kieselguhr as in the case of aluminium, thorium and ferric nitrates. In the second place the use of ammonia as precipitant is precluded and it was found that NaOH even in very dilute solution could not be used owing to the great tendency of both oxides to adsorb OH ions. In the third place a remarkable difference was found between the properties of these two oxides which necessitated the adoption of entirely different methods of precipitating them in the presence of kieselguhr.

Satisfactory evidence of the adsorption of cobalt oxide was obtained by the slow addition of the exactly equivalent amount of sodium carbonate in 0.1 M. solution to a suspension of 10 g. of kieselguhr in 100 ml. of cobalt nitrate solution, the maximum concentration of which was 0.018 M. Adsorption only takes place at room temperature, mixtures

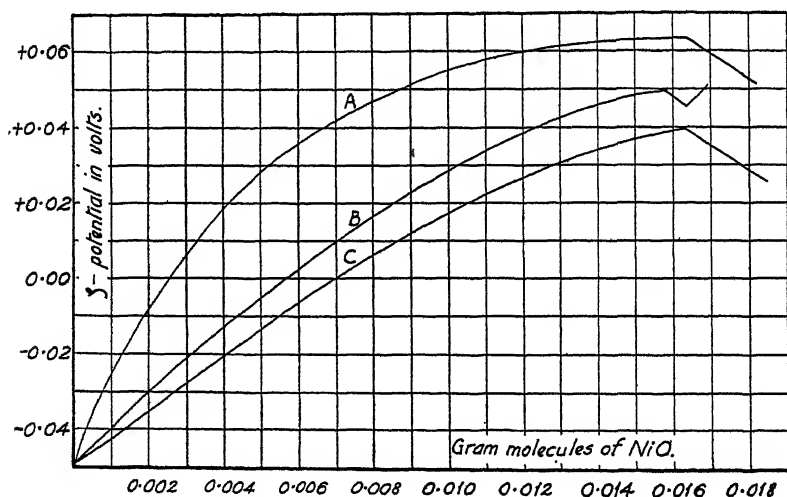


FIG. 4.

of kieselguhr and hydrated cobalt oxide being obtained when the sodium carbonate solution is added to a boiling suspension of kieselguhr in the cobalt nitrate solutions. The relation between the ζ -potential and the amount of CoO adsorbed on 100 g. of kieselguhr is shown by curve C in Fig. 3 and the maximum value of +0.01936 volt is obtained when exactly 0.0158 g. mol. of CoO has been adsorbed. The linear relation clearly indicates that, whatever the molecular units are, these units are progressively adsorbed until the kieselguhr is completely coated by them.

When the same method was used with nickel nitrate, the relation between the ζ -potential and the amount of NiO adsorbed was expressed by the very pronounced curve A in Fig. 5. There was, however, little doubt that 100 g. of kieselguhr are completely coated by 0.01632 g. mol. of NiO. Valuable information was obtained as to the nature of the adsorbate when the maximum concentration of the nickel nitrate solution was reduced to 0.0018 M. and the equivalent volumes of 0.1 M. sodium carbonate solution were diluted to 1 l. before addition to the

kieselguhr suspension. The ζ -potential relation then obtained is shown by the curve in Fig. 5 which indicates that the NiO is progressively adsorbed in three uni-molecular layers. Owing to the fact that a small quantity of nickel remained in solution as the bicarbonate this curve gives no accurate value of the amount of NiO required completely to coat the kieselguhr.

In order to overcome this source of error the same concentrations of the reactants were used and the kieselguhr suspension was boiled during the slow addition of the sodium carbonate solution. The ζ -potential relation then obtained is shown by curve B in Fig. 4, which is of some interest since, although the curvature is markedly less than that of curve A, it shows a sudden minimum when 0.01632 g. mol. of NiO has been adsorbed. The existence of this minimum was confirmed many times and was remarkable in view of the evidence previously obtained that 100 g. of kieselguhr completely coated by 0.01632 g. mol. had a maximum ζ -potential.

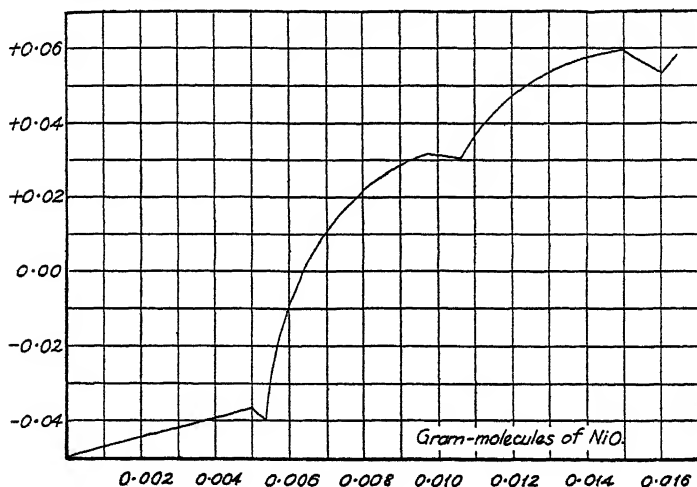


FIG. 5.

In view of the fact that the ideal linear ζ -potential relation found with CoO was not yet obtained, four improvements were made in the method of precipitation of NiO. In order to minimise the danger of the presence of OH ions, potassium bicarbonate was substituted for sodium carbonate and the concentration of nickel nitrate in the kieselguhr suspension was kept constant during the addition of the alkali. Furthermore, the concentration of the reactant solutions was reduced to one-half and the alkali solution was added exceedingly slowly to the vigorously boiling suspension in order to minimise the danger of the presence of nickel bicarbonate.

Two equal volumes of an exactly 0.1 M. nickel nitrate solution were diluted each to 2 l. An equal volume of an exactly 0.2 M. solution of Merck's pure crystallised potassium bicarbonate was also diluted to 2 l. In 100 ml. of one of the dilute nickel nitrate solutions 10 g. of kieselguhr were de-flocculated and the suspension transferred to a 4 l. enamelled iron saucepan resting on a powerful gas ring burner, after which the remaining 900 ml. were added. The electrically driven stirrer was then fixed into position near the bottom and to one side of the saucepan and

was driven so as to direct the suspension downwards. The suspension was then boiled vigorously for 10 minutes in order completely to de-aerate it.

Two burettes of the design shown in Fig. 1, one containing the second dilute nickel nitrate solution and the other containing the dilute potassium bicarbonate solution, were then fixed in position so that the ends of their capillary delivery tubes were immediately above the blades of the stirrer, one on each side of its central axis. The two solutions were added at an equal rate of 4 drops a second, measured at the jets just below the stop-cocks of the burettes. The time taken for the addition of the two solutions was about 3 hours. It was, of course, necessary to add boiling water from time to time to the suspension in order to keep the volume approximately constant. This water had previously been boiled in pyrex flasks in order completely to de-aerate it. When the whole of the nickel and alkali solutions had been added, the suspension was boiled for a further 20 minutes, after which the coated kieselguhr was collected on a 4-in. Buchner funnel, washed with 1 l. of water and dried overnight at 60°.

Very many preparations were made by this method and it was found that after a time the 0.2 M. KHCO_3 solution had dissolved sufficient silica from the walls of glass flasks to produce abnormal results. It is necessary, therefore, that this solution be kept in a quartz flask.

The relation now found between the ζ -potential and the amount of NiO adsorbed on 100 g. of the kieselguhr is expressed by curve C in Fig. 5. This curve is the nearest approach to the ideal linear relation which we were able to obtain, but it definitely proves that 100 g. of the kieselguhr are completely coated by exactly 0.01632 g. mol. of NiO as compared with 0.0158 g. mol. of CoO.

In order to determine the amount of hydration of the adsorbed CoO, 37.250 g. of the completely coated kieselguhr were first heated at 120° under reduced pressure in order to dry it, evidence having been previously obtained that neither the hydrated oxide nor the hydrated carbonate is decomposed to the oxide under these conditions. A weighed tube containing phosphoric oxide was then attached to the apparatus which was once again evacuated and the temperature was raised to 300° and maintained at that temperature for 3 hours. The amount of water collected was 0.0353 g. or 0.001961 g. mol.

Now 0.0158 g. mol. of CoO weighs $0.0158 \times 74.94 = 1.1851$ g. and, therefore, 100 g. of kieselguhr when completely coated weigh 101.1851 g. The weight of CoO in 37.250 g. of the coated kieselguhr is $1.1851 \times 37.250 / 101.1851 = 0.44644$ g. or 0.00582 g. mol. It follows that the number of water molecules associated with the adsorbed CoO molecules is in the ratio of 1 H_2O : 3 CoO.

It has already been proved that when 100 g. of the kieselguhr are coated with 0.01632 g. mol. of NiO the coating consists of three uni-molecular layers and there can be no doubt that the same is true when the coating consists of CoO. No other condition is possible in view of the close similarity between the amounts of the two oxides which completely coat 100 g. of the kieselguhr. It thus becomes evident that in the case of cobalt the adsorbate consists of three layers of anhydrous CoO and that on the outer surface, after drying at 120° under reduced pressure, there remains adsorbed a uni-molecular layer of water. Since CoO crystallises in the cubic (NaCl) system, the adsorbate is a lattice consisting of the crystal unit cells of CoO.

It is now possible to calculate the true surface area of the kieselguhr from the fact that 0.0158/3 g. mol. of CoO completely coats 100 g.

with a single uni-molecular layer. The molecular diameter of crystalline CoO is 4.24×10^{-8} cm. and hence the area covered by two molecules is $(4.24 \times 10^{-8})^2 = 1.798 \times 10^{-15}$ sq. cm. The number of groups of two molecules is $3.03 \times 10^{23} \times 0.0158/3 = 1.596 \times 10^{21}$ and hence the surface area is $1.798 \times 10^{-15} \times 1.596 \times 10^{21} = 2.869 \times 10^6$ sq. cm.

Applying the same method to NiO, the molecular diameter of which in the crystal lattice is 4.172×10^{-8} cm., the area covered by two molecules is $(4.172 \times 10^{-8})^2 = 1.7406 \times 10^{-15}$ sq. cm., and the surface area of 100 g. of the kieselguhr is $1.7406 \times 10^{-15} \times 3.03 \times 10^{23} \times 0.01632/3 = 2.869 \times 10^6$ sq. cm. Since these two values are in agreement, the value of 2.869×10^6 sq. cm. may be accepted as the effective surface area of 100 g. of the kieselguhr.

An interesting result was obtained when measurements were made of the adsorptive power of the kieselguhr towards both CoO and NiO in the presence of a small quantity of ThO₂. In a previous investigation it was found that when the hydrated carbonates of these metals were precipitated in the presence of thorium nitrate the ζ -potential of the products was a periodic function of their ThO₂ content. Furthermore, it was found that the ζ -potential had minimum values when the molecular ratio was 1 ThO₂ : 24 \times 1, 2, 3, etc. NiO or CoO and hence it was decided to determine the effect on the covering power of NiO and CoO when ThO₂ is present in the molecular ratio of 1 : 24.

No difficulty was experienced in coating kieselguhr with CoO containing ThO₂, the same method being used as in the absence of ThO₂. Owing to the very great dilution necessary in the case of NiO, it was not possible to suspend the kieselguhr in a solution containing Th(NO₃)₄ because practically the whole of the ThO₂ would at once be adsorbed on the kieselguhr. It was necessary, therefore, to add to the boiling suspension of kieselguhr in very dilute Ni(NO₃)₂ solution a very dilute solution of the requisite amounts of KHCO₃ and Th(NO₃)₄. It was found that these alkaline thorium solutions were sufficiently stable, provided that they were freshly prepared from a concentrated Th(NO₃)₄ solution to which strong HNO₃ had been added and that the containing vessels had been cleaned with strong HNO₃ and washed with water before use. It was expected that the stability of the solutions would be increased by saturation with CO₂, but it was found that CO₂ at once precipitated with ThO₂. The same phenomenon was observed in the case of iron, since CO₂ quantitatively precipitates hydrated Fe₂O₃ from a very dilute solution of Fe(NO₃)₃ which has been neutralised with ammonia.

In each preparation one-half the necessary volume of the Th(NO₃)₄ solution was measured by means of a micro-burette and diluted to 500 ml., and one-half the necessary volume of 0.2 M. KHCO₃ solution was also diluted to 500 ml. and these two solutions were mixed. In every other respect the procedure was the same as that already described for coating the kieselguhr with pure NiO. When the first half of the alkaline thorium solution had nearly all been added to the boiling kieselguhr suspension, the second half was prepared as above and added to that remaining in the burette.

It was noted that during the washing of the preparations in which the kieselguhr had been almost completely or completely coated they become grey-black on the surface. This darkening was very pronounced when the coating had been successfully carried out.

The relation between the ζ -potential and the amount adsorbed of CoO containing ThO₂ is linear as in the case of pure CoO shown by curve C in Fig. 3, but it was found that 100 g. of kieselguhr are coated

by 0.01354 g. mol. of CoO + 0.01354/24 g. mol. of ThO₂ as compared with 0.0158 g. mol. of pure CoO.

In the case of NiO containing ThO₂ the ζ -potential relation is shown by curve B in Fig. 3. This curve is almost linear and indicates that 100 g. of kieselguhr are completely coated by 0.0140 g. mol. of NiO + 0.0140/24 g. mol. of ThO₂ as compared with 0.01632 g. mol. of pure NiO.

Now $0.01354 \times 7/6 = 0.0158$ and $0.0140 \times 7/6 = 0.01632$ and it follows from this that the covering powers of CoO and NiO are each increased by one-sixth when they contain ThO₂ in the molecular ratio of 1 ThO₂: 24 CoO and 1 ThO₂: 24 NiO, respectively. It is evident, therefore, that 1 molecule of ThO₂ must replace one group of 4 Co and 4O atoms in the one case and 4 Ni and 4O atoms in the other case out of every seven such groups and that this replacement must take place in each of the three layers of the crystal lattice.

It has already been shown that the diameter of the ThO₂ molecule in a unimolecular layer adsorbed on kieselguhr is 5.72×10^{-8} cm. The side of the square area occupied by 4 Co and 4O atoms in a single lattice layer is 5.996×10^{-8} cm. and in the case of NiO this dimension is 5.90×10^{-8} cm. It would appear, therefore, that 1 ThO₂ molecule can only enter each lattice layer by replacing 4 Co and 4O or 4 Ni and 4O atoms.

There remains to be explained the observations made during the development of the method of coating kieselguhr with pure NiO. The curves A, B and C in Fig. 4 show that as the method was improved the curvature of the ζ -potential relation became less pronounced and the ζ -potential of kieselguhr completely coated with 0.01632 g. mol. of NiO decreased from +0.063 volt to +0.040 volt. Then again, when the NiO contained ThO₂ in the molecular ratio of 1 ThO₂: 24 NiO the ζ -potential relation became nearly linear and reached a maximum value of +0.030 volt when the kieselguhr was completely coated.

Now a determination by the method previously described in the case of kieselguhr completely coated with CoO of the water content of the kieselguhr completely coated with pure NiO and having the ζ -potential of +0.060 volt showed that there were present 3.6 unimolecular layers of water. A similar determination with the kieselguhr completely coated with NiO containing ThO₂ and having a ζ -potential of +0.030 volt showed that the adsorbate was anhydrous. It is evident, therefore, that high values of the ζ -potential indicate the presence of water within the adsorbed NiO.

It is important to note that the curves A, B and C in Fig. 4 indicate that in spite of water being present in the NiO the amount of NiO which completely coats 100 g. of kieselguhr remains constant at 0.01632 g. mol. It follows from this that when the adsorbate contains water this water must be adsorbed in between uni-molecular layers of anhydrous NiO. Furthermore, the very pronounced curvature of the ζ -potential relation proves that the amount of the intra-molecular layers of water is a maximum when small quantities of NiO have been adsorbed and decreases to a minimum when 0.01632 g. mol. has been adsorbed. If this were not true a linear ζ -potential relation would have been obtained. It becomes necessary, therefore, to recognise the existence of a close-packing effect, the influence of which reaches a maximum when the kieselguhr is completely coated with NiO. This close-packing effect is very strikingly shown by curve B in Fig. 5 which indicates that when

the effect is a maximum a minimum value of the ζ -potential can be obtained.

Curve B in Fig. 3 shows that when NiO containing ThO₂ in the molecular ratio of 1 ThO : 24 NiO is adsorbed by kieselguhr the ζ -potential relation is almost linear and that the ζ -potential of the completely coated kieselguhr is +0.030 volt which is smaller than the lowest value of +0.040 volt obtained in the absence of ThO₂. There can be no doubt, therefore, that the presence of the ThO₂ molecules materially aids the close packing of the NiO lattice which then in fact becomes anhydrous.

Conclusions.

1. Pure kieselguhr adsorbs the anhydrous oxides of aluminium, thorium, nickel and cobalt.
2. The adsorbate in each case is activated as the result of the formation of adsorption complexes.
3. In the cases of the oxides of aluminium and thorium the adsorption is restricted to a single unimolecular layer.
4. In the cases of the oxides of nickel and cobalt there are adsorbed three unimolecular layers together forming a single layer of crystal unit cells.
5. When a mixture of nickel and thorium oxides in the molecular ratio of 1 ThO₂ : 24 NiO is adsorbed, one out of every seven groups of 4 Ni and 40 atoms in each of the three layers of the crystal lattice is replaced by a molecule of ThO₂. This is also true when CoO is substituted for NiO.

Our thanks are due to Mr. J. W. Ireland for the valuable assistance he rendered during this investigation.

A THEORY OF THE FORMATION OF PROTECTIVE OXIDE FILMS ON METALS.

By N. F. MOTT.

Received 1st June, 1939.

Many metals when exposed to air develop an oxide film on the surface, the thickness x of the film increasing with the time according to the parabolic law

$$x^2 = \text{const. } t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For others, notably aluminium, the film develops according to the parabolic law only up to thicknesses of the order of 10^{-6} cm., and then virtually stops growing. Some experimental results showing this are reproduced in Fig. 1. The purpose of this note is to suggest a theory of this interrupted growth.

The parabolic law is accounted for in, for example, the oxidation of zinc, as follows :¹

At the metal-oxide interface metal atoms go into solution in the oxide, there dissociating into interstitial ions and free electrons in the

¹ Cf., for example, C. Wagner and K. Grünewald, *Z. physik. Chem., B*, 1938, 40, 455.

conduction band of the oxide. If the concentration of such atoms is n per cubic centimetre at the interface where there is equilibrium between metal and oxide, and zero at the interface between oxide and gas, there will be a concentration gradient n/x in the oxide film. If D is the diffusion coefficient of the ions,* the flow of atoms is Dn/x per second across unit area. Thus if Ω is the volume of the oxide per metal ion

$$\frac{dx}{dt} = \frac{2\Omega Dn}{x},$$

giving

$$\frac{1}{2}x^2 = 2\Omega Dnt.$$

In other cases (e.g. the oxidation of copper) oxygen is dissolved at the oxide-gas interface; our theory is however only applicable to cases of the former type.

Let us assume that the oxide is an insulator when of stoichiometric composition, i.e. that it contains no interstitial ions or electrons. Then the concentration n of (dissociated) atoms in the layer next to the metal will be given by a formula of the type

$$n^2 = A^2 \exp\{- (W_1 + W_2)/kT\}.$$

Here $1/A$ is of the order of the volume of the unit cell of the oxide, W_1 denotes the energy required to bring an electron from the metal into the

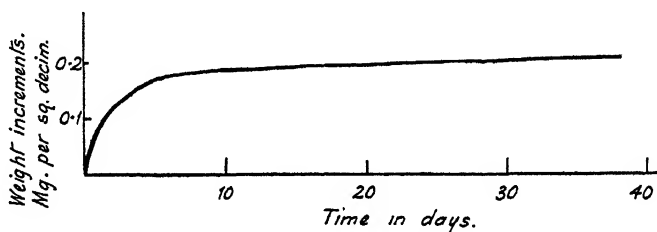


FIG. 1.—Oxidation of aluminium at ordinary temperatures, showing weight increment per sq. decimetre of surface. The aluminium was exposed to unpurified city air (from W. H. J. Vernon, *Trans. Faraday Soc.* 1927, 23, 152).

conduction band of the oxide, and W_2 the energy required to bring an ion from the metal into an interstitial position in the oxide.

If $W_1 + W_2$ is too large, n will be negligibly small and the oxide film cannot grow. Suppose, however, that $W_2 < W_1$, so that at the temperature considered ions can pass from the metal to the oxide until prevented by the space charge set up, but no electrons have enough energy to be excited into the conduction band of the oxide. Then, although a thick film cannot grow, if the film is sufficiently thin, electrons can pass through it by the quantum mechanical tunnel effect. We suggest that this is what happens in the case of oxide films on aluminium. The penetrability of a film to electrons is extremely sensitive to thickness, a few atomic layers making all the difference between easy transparency and complete opacity. Thus we expect a parabolic law of growth up to a certain thickness—of the order 0.5×10^{-8} cm. and then a rather sudden stop.

We shall now make an estimate of the maximum thicknesses obtainable according to this theory. The number of electrons per second

*The flow is determined by the diffusion coefficient of the ions; the much more mobile electrons can always keep up with them.

which are excited into the conduction band will be given by the ordinary formula for thermionic emission

$$\frac{120 T^2}{q} e^{-W_1/kT} \text{ per cm.}^2 \text{ per sec.}$$

where q is the electronic charge in coulombs. At 300°C. this gives

$$A e^{-W_1/kT} \quad A \sim 0.7 \times 10^{26}.$$

To form a new layer of atoms about 10^{15} electrons per cm.^2 are required, so the time taken to form one layer is about

$$10^{-11} e^{W_1/kT} \text{ sec.}$$

If we put this equal to a year ($\sim 10^7$ sec.) we obtain

$$W_1 \sim 42 \times 300 k \sim 1 \text{ e.v.}$$

With values of W_1 of this order of magnitude, then, there can be practically no growth without tunnel effect, however small W_2 may be.

The number penetrating the barrier by means of the tunnel effect is ²

$$A' \exp. \left\{ -2x \sqrt{\left(\frac{2mW_1}{\hbar^2} \right)} \right\},$$

where A' is the same order of magnitude as A . If the tunnel effect gives a greater current than thermionic emission, we must have

$$2x \sqrt{\left(\frac{2mW_1}{\hbar^2} \right)} < \frac{W_1}{kT},$$

or

$$x < \frac{1}{2} \frac{\hbar}{kT} \sqrt{\left(\frac{W_1}{2m} \right)}.$$

If $W_1 = 1 \text{ e.v.}$, this gives

$$x < 0.4 \times 10^{-6} \text{ cm.}$$

Thus the order of magnitude of the thickest film which can be built by tunnel effect is 40 Å.

The density of Al_2O_3 is between 3.7 and 4.0.³ Taking the latter value, we see that the mass of a layer 40 Å. thick is 0.16 mgm. per sq. decim.; of this the mass of oxygen is 0.075 mgm. per sq. decim. This is of the same order of magnitude as the observed increment, shown in Fig. 1, of 0.2 mgm.; the difference may well be accounted for by the corrugated nature of the surface of a metal sheet.

We may note that a film which cannot grow for one oxidising agent may be able to grow rapidly for another. The theory given here postulates that the oxide in equilibrium with oxygen is of stoichiometric composition. For some other oxidising agent this might not be the case; if the oxide layer can absorb oxygen, the reaction can proceed, even though the metal is insoluble in the oxide.

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² Cf., for example, J. Frenkel, *Physic. Rev.*, 1930, 36, 1604.

³ Landolt-Börnstein's Tables, Vol. I.

THE STRUCTURE AND PROPRIETIES OF HIGHLY PURIFIED REDUCTION GOLD SOLS.*

BY WO. PAULI, J. AND ST. SZPER.

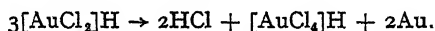
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The constitution of colloidal gold has been elucidated from previous experiments on spark dispersed sols,¹ prepared by dispersion of a gold wire in dilute HCl, and concentrated by electro-decantation (E.Dec.), whereby really concentrated purified gold sol was obtained for the first time. Thus, by specially developed analytical methods the charging groups were characterised as chloro-complexes and H⁺ ions as *Gegenionen*.

Similar experiments on reduction gold sols, purified and concentrated in the same manner, gave apparently more complicated and contradictory results, which were eventually found to be due to a diminution of the charge density and a hydrolytic sensibility of the chloro-complexes.

It was of interest to carry out further experiments on reduction gold sols in order to complete these investigations.

Pauli, Russer and Brunner² experimented with gold sols, obtained both by reduction with phosphorus (a method used by Faraday) and by reduction³ with H₂. Laborious pioneering experiments have already been made with the formalin gold sol. The results can be summarised as follows. A pure dispersion chloro-sol has as its charging ionogenic group [AuCl₂]⁻H, which, when the sol is frozen, goes into solution and forms HCl and [AuCl₄]⁻H according to the equation:



By further electrodecantation, hydrolysis of AuCl₂H occurs, with formation of the [AuCl(OH)]⁻H complex. The latter complex produces, on going into solution, only gold oxide and HCl. Reduction gold sols purified by E.Dec. readily give sols with such chloro-hydroxy mixed complexes. The chloro gold sols are stable to boiling and to the action of CO₂, but when they are transformed into sols with chloro-hydroxy mixed complexes they lose this property.⁴

The following experiments were made on a gold sol obtained by reduction with ethyl alcohol. A new method of obtaining 2.5 litres or more in one operation with a concentration of 50 mg. Au per litre is described.

Gold chloride was reduced at 60° C. in slightly alkaline solution. The time between the first appearance of a slight pink colour and the development of a deep red is about 15 minutes. For preparation of a sufficient quantity of concentrated gold sol with 2.3 g. Au per litre about 20 litres of solution are needed.

* These experiments were carried out at the Institute for Medical Colloid Chemistry of the University of Vienna in 1937.

¹ Wo. Pauli and E. Russer, *Kolloid Z.*, 1932, 58, 22; a summary of the history and the subsequent work is given by Pauli, *Naturwiss.*, 1932, 20, 551.

² Wo. Pauli, E. Russer and E. Brunner, *Kolloid Z.*, 1935, 72, 26.

³ L. Fuchs and Wo. Pauli, *Kolloid Beih.*, 1925, 21, 195.

⁴ F. Eirich and Wo. Pauli, *ibid.*, 1930, 30, 113.

The sols were concentrated by electro-decantation.¹ The theory of the process is described by Blank and Valko.⁵ The concentration of the colloidal particles increases on one of the membranes in a microlayer, while on the other a colloid-free microlayer is formed. The density difference makes the concentrated sol flow to the bottom of the electro-dialyser, while the liquid on the other side rises and forms an upper, colloid-free layer. The process is the more rapid as the sol becomes purer, because the greater part of the current is in this case carried by the colloidal particles. The working voltage of the old type of electro-dialyser is from 6 to 8 v. An electro-dialyser newly designed by W. P. permits an increased voltage (200 to 250 v.) to be used, thus speeding up the decantation process considerably. The new design differs in principle in that the sol is removed from the electrical field, immediately after concentration. Thus the particles of the concentrated sol no longer transport the current and the sol therefore undergoes no further electrolysis. Furthermore, the process can be made continuous by the continual supply of the initial sol to the middle cell of the electro-dialyser and by simultaneous removal of the clear and colourless top layer. It is possible by this method to concentrate 4 to 5 litres of a sol to 100 or 150 c.c. in about 10 hours.

Preparation of the Sols.

1500 c.c. of conductivity water were heated to 50-60° C. in a Murano or Jena 3 l. flask. At this temperature 50 c.c. of 0.5 % gold chloride solution and 22 to 24 c.c. of 0.18 N. K_2CO_3 solution were added. The slightly yellow solution became colourless after a few minutes. At this point 50 to 80 c.c. of 96 % alcohol were added little by little. In about 10 minutes the solution became pink and then gradually darkened to red. In a few cases, however, the solution assumed a slight blue tinge. When a satisfactory deep red was attained, 1000 c.c. of conductivity water were added and the flask cooled. Some experience is necessary to determine the correct proportion of K_2CO_3 and the right time for the addition of water, as these factors affect the particle size.

The specific conductivity of a freshly prepared sol was 1.25×10^{-4} mho., the gold content being about 50 mg. per litre.

The sol so prepared was placed in an electro-dialyser with a middle cell of 1500 c.c. capacity and a collecting vessel of 250 c.c. A potential of 110 v. was applied, and thus 20 litres were concentrated to 250 c.c. in four days. The purification was not complete when such a rapid concentration was applied only once. The final purification was effected in a small electro-dialyser with a middle cell of 400 c.c. and a voltage of 10-15 volts. Table I (a) gives the progress of the purification of the sol A_1 .

After five successive electro-decantations, substituting each time the top layer by conductivity water, the conductivity of the top layer was 2.3×10^{-6} mho., which is quite satisfactory. The gold content of the sol was, however, too small, and the operation was repeated. It must be remembered that a reduction gold sol has initially as *Gegenionen* not H^+ but K^+ ions, and for this reason the conductivity calculated from the concentration of hydrogen ions (κ_H) smaller than that obtained by direct determination (κ) there being in the solution both K^+ and H^+ ions.

The transition from K^+ to H^+ ions sol (or transition of a colloid salt into a colloid acid) was observed by Pauli and Kautsky⁶ in 1923, who explained it by hydrolysis on the membrane. This was used as a general method

⁵ F. Blank and E. Valko, *Biochem. Z.*, 1928, 195, 220.

⁶ E. Kautsky and W. Pauli, *Kolloid Beih.*, 1923, 17, 294.

for preparation of hydrophobic and hydrophilic acidoid sols. The improvement of the electro-decantation process allows this process of changing the *Gegenionen* to be brought about and to be followed more closely.

Table I (b) gives the figures for a similar purification process of sol A_2 . The figures show clearly that the difference between κ and κ_H is smaller after each decantation. After six successive decantations the K^+

TABLE I.

E. Decanta- tion.	$\kappa \times 10^6$, Top Layer.	$\kappa \times 10^6$, Gold Sol.	$\kappa_H \times 10^6$.	$H_{littr.} (10^{-5}N)$.	Gold Content (g.l.)
A. Purification of Sol A_1.					
1	16.0	—	—	—	—
2	11.0	—	—	—	—
3	4.40	—	—	—	—
4	4	1.95	—	—	—
5	2.3	1.66	—	—	0.40
6	3.5	2.48	1.34	3.57	1.05
7	1.75	1.82	1.20	3.19	1.15
B. Purification of Sol A_2.					
1	—	—	—	—	—
2	—	—	—	—	—
3	2.3	3.16	1.17	3.13	1.497
4	3.0	2.04	1.17	3.13	—
5	2.3	—	—	—	—
6	1.4	1.21	1.15	3.08	1.021
7	3.1	4.22	1.42	3.8	—
8	2.9	2.35	1.84	4.9	1.775
9	2.6	1.4	0.91	2.44	1.22
C. Purification of Sol A_3 with addition of Acetic Acid.					
1	37.00	12.8	—	—	0.61
2	20.00	7.6	—	—	0.71
3	9.00	3.0	—	—	0.50
4	5.00	2.85	3.04	8.10	0.55
5	4.3	3.23	3.29	8.78	1.07
6	4.00	2.25	2.28	6.08	0.66
7	3.00	1.93	1.52	4.05	1.02
8	2.60	1.90	1.61	4.3	1.85

ion content was practically zero. At this point a new portion of concentrated but not purified sol was added. The κ and κ_H values after the seventh E.Dec. diverged again. The difference became smaller again after two more decantations.

To shorten the time of the exchange of K^+ to H^+ a small quantity of acetic acid (final concentration 1×10^{-3} N.) was added to the sol A_3 . The resulting figures are given in the Table I (c). It will be seen that after four electro-decantations all the K^+ ions were exchanged, but that the excess acetic acid was removed only very slowly.

It was noticed that the sol with K^+ ions as *Gegenionen* can be concentrated, without harm, to a content of 50 g. or more per litre, although under such conditions acidoid sols would be entirely coagulated. This is due to the fact that not only the sols, but also the *Gegenionen* are concentrated. The threshold value of H^+ ions is about 1×10^{-4} N., and that of K^+ ions about 1×10^{-2} N., therefore, when the K^+ ions are present as *Gegenionen* their concentration can be much greater than that of the H^+ ions, without causing coagulation of the sol.

For instance, in the last but one decantation of sol A_2 , the volume of the sol (bottom layer) was only about 5 c.c. On dilution to 250 c.c., a gold content of 1.225 g./l. was found, corresponding to 70 g./l. for the original 5 c.c. The sol A_4 was concentrated to 10 c.c. and then diluted to 300 c.c. This was found to have a gold content of 1.885 g./l., corresponding to 66 g./l. for the original 10 c.c.

This explanation was confirmed by the results of freezing experiments. Purified concentrated spark-dispersed sols coagulate after 2 to 3 hours at -9° C. Reduction gold sols, however, especially those with a high K^+ content, must be frozen several times before coagulation occurs.

Characteristic of the Sols.

To characterise and define the sols, conductivity determination, conductometric titrations of H^+ and Cl' , and glass-electrode potential measurements of the sol and of the liquid remaining after the freezing of the sol (F.L.), were carried out according to the methods of Pauli and collaborators.¹ The concentration of H^+ ions of sufficiently purified sol gives the corresponding concentration of *Gegenionen*. The composition of the charging groups can be ascertained by determination of chlorine before (Cl_d) and after (Cl_r) reduction with H_2O_2 of the liquid remaining after freezing the sol. Table II. gives the characteristic figures for five reduction gold sols. It will be seen that the constitution of the reduction gold sols is similar to that of the spark dispersed sols. For sols A_1 , A_2 , A_3 and A_5 the respective values of κ are in each case larger than those of κ_H . There were in the sols, therefore, not only H^+ but also K^+ ions. In sol A_4 , however, where κ and κ_H are equal the sol contains H^+ ions only. The concentration of K^+ ions in the other sols can be calculated indirectly. The difference $\Delta\kappa$ between (κ) and (κ_H) is due to the K^+ ions. Taking $A_{\infty}^{K^+} = 76$, which is permissible for such small concentration of K^+ , the calculation of the concentration of K^+ from the $\Delta\kappa$ gives reasonable values. These are given in the Table II. as K^+_{calc} .

The liquid remaining after freezing the sol had a similar composition to the sols described in previous papers.¹ In the reaction

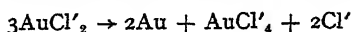


TABLE II.

Sol.									F.L.			
Sol.	Au g per litre.	M_{Au} ($10^{-5}N$).	$\kappa \times 10^6$ Top Layer.	$\kappa \times 10^6$ Sol.	$\kappa_H \times 10^6$.	$H_{lit.}$ ($10^{-5}N$)	K' calc. ($10^{-5}N$)	C. Eq.	$\kappa \times 10^5$.	Cl_d ($10^{-5}N$)	Cl_r ($10^{-5}N$)	Cl_d/Cl_r
A ₁	1.15	5.75	1.75	18.2	14.7	3.92	1.75	101	2.2	6.0	—	—
A ₂	1.6	8.0	2.5	69.8	59.6	15.9	7.7	35	8.8	16.0	45.0	1:2.9
A ₃	1.22	6.1	2.9	14.0	9.15	2.44	1.95	139	1.08	3.8	10.0	1:2.6
A ₄	1.85	9.25	2.6	19.0	16.1	4.3	—	215	2.0	2.3	6.5	1:2.8
A ₅	1.14	5.7	2.0	53.5	46.9	12.5	4.6	33	5.21	—	—	—

2HCl corresponds to 1HAuCl₄. In the case of sol A₄ we found for the total concentration of chlorine (Cl_r) a value of $6.5 \times 10^{-5} N$. A third of this ($2.2 \times 10^{-5} N$) corresponded to the Cl' of the free HCl. The rest ($4.35 \times 10^{-5} N$) was derived from HAuCl₄ corresponding to $1.1 \times 10^{-5} N$. aurochloric acid.

On the other hand, on titrating with NaOH the liquid remaining after freezing the sol, H⁺ ions both from HCl and HAuCl₄ are neutralised, and one of the chlorine atoms in the AuCl₄ complex is exchanged for OH. The quantity of NaOH necessary is thus:

$$2.2 \times 10^{-5} + 1.1 \times 10^{-5} + 1.1 \times 10^{-5} = 4.4 \times 10^{-5} N.$$

Direct titration gave $4.6 \times 10^{-5} N$, which is satisfactorily close.

These calculations plainly indicate that reduction gold sol is a typical chlorosol, whose constitution does not differ from the spark dispersed gold chloro-sols. Further evidence is provided by the quotient Cl_d/Cl_r , which is very nearly 1/3.

For sols containing both K⁺ and H⁺ ions as *Gegenionen* such simple calculations cannot be done. The determination of the amounts of K⁺ and H⁺ and, therefore, of the quantities of the respective ionogenic groups KAuCl₂ and HAuCl₂ presents difficulties. From the amounts of Cl_d and Cl_r we obtain only the sum of H⁺ + K⁺. The proportion of Cl_d to Cl_r being nearly 1 to 3, there is no doubt that the sols have auro-complexes as charging groups. The values of Cl_d/Cl_r were slightly smaller than required for a pure chloro sol. This shows that our sols were slightly contaminated by the chloro-hydroxy mixed complexes.

The largest difference was shown by the sol A₃, in which the value for Cl_d/Cl_r was 1/2 instead of 1/3. This means that the sol contained a larger quantity of chloro-hydroxy complexes. These mixed auro-complexes gave no increase of Cl by reduction of the liquid remaining after freezing the sol. Such sols are formed, as stated by Pauli, through hydrolysis of chloro-complexes, and are not stable towards boiling. CO₂ action gives also a coagulation of such a sol.³ As a matter of fact, the sol A₃ was not stable towards boiling, and was partially coagulated by CO₂ after several hours.

The concentration of H⁺ ions in the sol A₅ was determined both by conductometric titration and by potentiometric measurement.

Table III. gives the value of the concentration of H^+ ions determined with a glass electrode as a_H and that by the conductometric titration as $H_{titr.}$. There was

TABLE III.—Sol A_3 .

	$\kappa \times 10^5$.	$H_K (10^{-5} N.)$	$H_{titr.} (10^{-5} N.)$	$a_H (10^{-5} N.)$
Sol	5.35	13.4	12.5	12.6
F.L.	5.21	13.0	10.7	11.0

no difference between the values found by the conductometric titration and by the potentiometric measurement of active H^+ , either in the sol or in the liquid remaining after freezing the sol. The calculated H^+ ion concentration is much greater than that actually found, indicating the presence of K^+ ions.

The colloid equivalents of reduction gold sol were of the same order of magnitude as those of the spark dispersed sols. The colloid equivalent of a gold sol is defined as the ratio of the molarity of gold atoms (M_{Au}) to the activity of *Gegenionen*. For the pure acidoid sol A_3 the colloid equivalent (C.E.) is $M_{Au}/H_{titr.}$; for sols which contain also K^+

$$\text{ions C.E.} = \frac{M_{Au}}{H_{titr.} + K_{calc.}}$$

All our results for the reduction gold sols therefore correspond to the previous conception of chloro-aurous acid as the source of the charge.

Following the new development of the electro-decantation process, it is possible to obtain reduction gold sols which have only a slight content of chloro-hydroxy complexes as well as pure chloro-complexes.

The sols have been applied to the study of the protective action of some hydrophilic sols which will be communicated in a subsequent paper.

Summary.

1. A new method has been developed for preparing larger amounts of reduction gold sols by means of ethyl alcohol.

2. These gold sols were purified and highly concentrated by a newly perfected electro-decantation process.

3. Analysis of the sols and of the liquid obtained by freezing coagulation shows that the sols have, as charging ionogenic groups, auro-chloro complexes which can partially hydrolyse to mixed chloro-hydroxy complexes. The results are in full harmony with those obtained with other types of gold sols.

One of us (J. S.) desires gratefully to acknowledge the receipt of a grant from Feliks Wiślicki Foundation, Warsaw, which enabled this work to be carried out.

AN INFRA-RED STUDY OF HYDRAZOIC ACID, HN_3 .

By MANSEL M. DAVIES.

Received 22nd June, 1939.

It is desired to report a study of the absorption spectrum of hydrazoic acid, HN_3 , in the region $2\ \mu$ to $21\ \mu$ undertaken to elucidate its molecular structure.

The hydrazoic acid was prepared by the method described by Meyer.¹ This consisted in heating sodium azide with five times its weight of pure stearic acid in an evacuated glass apparatus. Kept in the gaseous state at 10 to 20 cm. pressure, the hydrazoic acid was quite stable, but one violent explosion with the condensed acid resulted in the experiments being abandoned before the work had been completed.

Using consecutively prisms of quartz, fluorite, and sylvine, the Hilger instrument D. 83 provided the general characteristics of the absorption

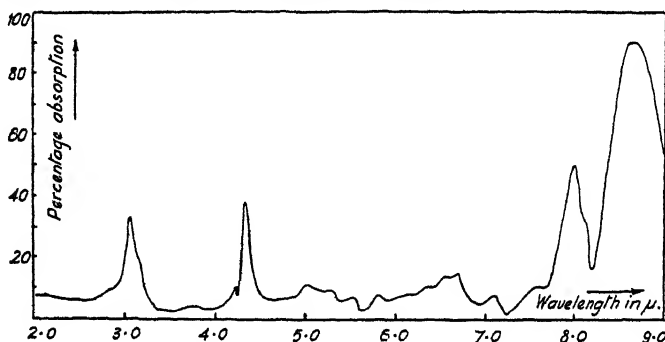


FIG. 1.—Infra-red absorption of hydrazoic acid. Path length = 11 cm.; Pressure = 11 cm.

spectrum. With this instrument, two absorption cells were used, one giving a path length of 11 cm.; the other, having an absorption path of 25 cm., was used only for the long-wave region (9 to $21\ \mu$). In these cases the curves reproduced show the percentage absorption corrected for that of the evacuated cell, which was usually determined both before and after measurements on the gas. Two of the bands have been examined under high dispersion with the grating spectrometer described by Sutherland, Lee and Conn.² Here the absorption path was always 26 cm., and it was thought sufficient to check that the cell transmissions were constant to within a per cent. or two over the limited regions examined: the corresponding curves have not been corrected for the cell absorption. The pressure of HN_3 has been indicated with the various results reproduced: usually it was near 10 cm.

Well-defined absorption bands were found in the regions of $3.0\ \mu$, $4.35\ \mu$, $4.7\ \mu$, $8.0\ \mu$, and $8.7\ \mu$; a much weaker absorption appears to have its centre near $18.5\ \mu$. It will be convenient to discuss the identity and nature of the different bands in this wave-length order. Fig. 1 shows

¹ Gunther, Meyer and Muller-Skjold, *Z. physik. Chem., A*, 1935, **175**, 154.

² To appear shortly.

the general aspect of the spectrum up to $9\ \mu$, and also serves to indicate the relative intensities of the bands.

The $3.0\ \mu$ Band.

This absorption was readily detected with the quartz prism instrument. There can be no doubt that it corresponds to the fundamental N—H valence vibration of the molecule. As the determination of the precise nature of this vibration should provide important evidence as to the form of the

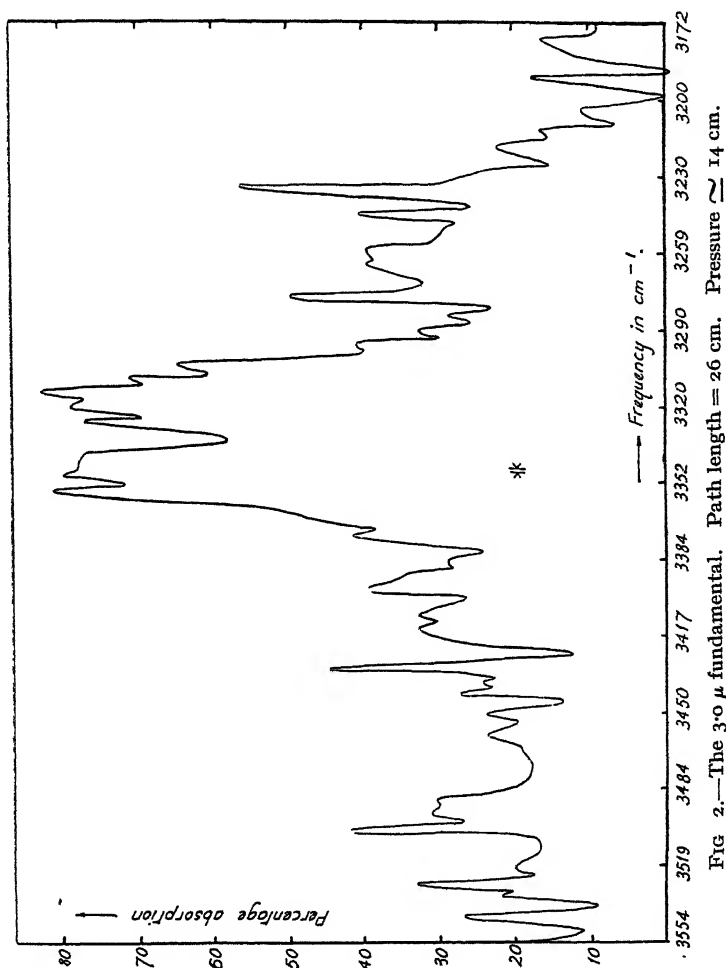
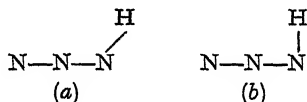


Fig. 2.—The $3.0\ \mu$ fundamental. Path length = 26 cm. Pressure = 14 cm.

molecule, the band was twice examined on the grating instrument with reasonable agreement between the results. Fig. 2 illustrates these. An intense central region is flanked on either side by a number of irregularly spaced sharp absorptions. The central absorption is easily shown to have a doublet form with a median frequency of $3336.2 \pm 1.6\ \text{cm}^{-1}$. This is practically coincident with the frequency of the valence N—H vibration in the ammonia molecule at $3335\ \text{cm}^{-1}$, proving the close similarity of the corresponding force constants in the two molecules.

The second and third overtones of this fundamental have been examined in the photographic region by Herzberg, Patat and Verleger.³ A comparison of Fig. 2 with Figs. 5a and 5b of Verleger's paper shows the general identity of the two absorptions. Dr. Verleger has been good enough to send the present author the actual frequencies and approximate intensities of the main peaks measured by him. A plot of the frequency differences of these peaks in the fundamental and its second overtone shows surprisingly little correspondence in the two cases, except for the peak absorptions in the central region. This lack of agreement may be due to the poorer resolution with which the $3\ \mu$ band was plotted: readings were taken every $1.7\ \text{cm}^{-1}$ or $3.4\ \text{cm}^{-1}$.

The general form of the band suggests that the absorption resembles that of a perpendicular vibrational band in a symmetrical top molecule. That this is only approximately so is shown by the almost complete irregularity in the spacings of the peaks resembling Q-branches. This irregularity extends to the overtone. Again, within the strong central region, Herzberg, Patat, and Verleger were able to resolve a much more regular line spacing of about $0.8\ \text{cm}^{-1}$ width. The most plausible interpretation of these results is that they arise from a valence N—H vibration which is a hybrid of the perpendicular and parallel types in a symmetrical top. There are good reasons for the supposition, which is later confirmed, that the three nitrogen atoms in the molecule lie in a straight line. In particular, Pauling and Brockway's analysis of the electron diffraction results for methyl azide,⁴ and Knagg's X-ray study of cyanuric triazide⁵ may be cited. In both these covalent structures, the N_3 group is found to be linear. It then follows from the appearance of this band that the N—H bond is inclined to the N—N line at an angle between, and not very near to, 0° and 90° . On these grounds the molecular form is best represented as shown in (a), the alternative (b) being ruled out as it would require the N—H valence vibration to be a simple perpendicular one in an almost symmetrical top, whereas the results show it to be of a "mixed" nature. The form (b) is also eliminated by the fine structure observed in the overtone.



The $4.36\ \mu$ Band.

Both from its intensity and position this band is clearly the first overtone of the fundamental at $8.7\ \mu$. The centres of these bands have the frequencies $2294 \pm 10\ \text{cm}^{-1}$ and $1150 \pm 10\ \text{cm}^{-1}$ respectively.

The $4.7\ \mu$ Band.

On the prism instrument this band had a 50 % peak absorption for $11\ \text{cm}$. of HN_3 in a $12\ \text{cm}$. cell. One of the determinations of its contour made on the grating instrument is shown in Fig. 3, together with another plot of the central Q-branch. The band centre is at $2139.6 \pm 0.3\ \text{cm}^{-1}$. The appearance of this band is typical of the unresolved structure corresponding to a parallel vibration in a symmetrical top. Accordingly, the nature and magnitude of this frequency agree with its assignment to the unsymmetrical valence vibration in the linear N_3 group. This is one of the two frequencies reported by Engler and Kohlrausch⁶ from their study of the Raman effect in liquid HN_3 . Actually their value for it is $2389\ \text{cm}^{-1}$.

³ *Z. Elektrochem.*, 1935, 41, 522; also Verleger, *Physik. Z.*, 1937, 38, 83.

⁴ *Proc. Nat. Acad. Sci.*, 1933, 19, 860; *J.A.C.S.*, 1937, 59, 13.

⁵ *Proc. Roy. Soc., A*, 1935, 150, 576.

⁶ *Z. physik. Chem., B*, 1936, 34, 214.

The wide discrepancy between this and the infra-red value may be partly accounted for by the uncertainty in the Raman value resulting from the

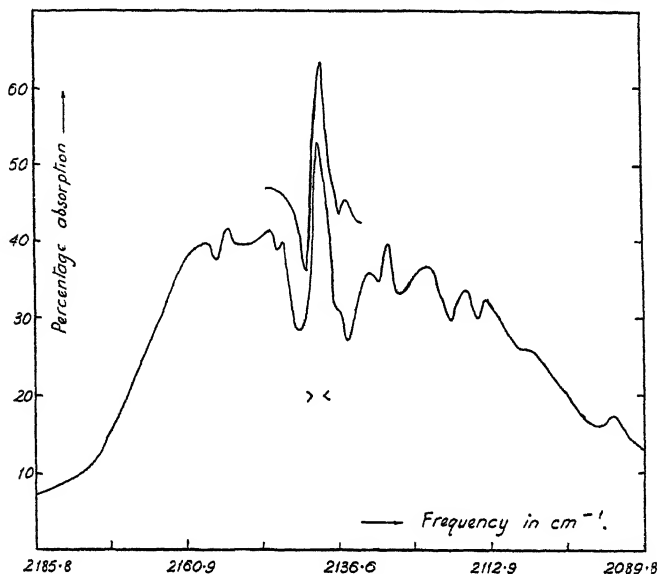


FIG. 3.—The $4.7\ \mu$ fundamental. 26 cm. cell. Pressure = 3 cm.

difficulty of the observations on the liquid. From the much more certain results for methyl azide, Kahovec, Kohlrausch, Reitz and Wagner ⁷ have identified the same frequency in CH_3N_3 as $2104\ \text{cm}^{-1}$. It is unlikely that this frequency would change very much in the species HN_3 and CH_3N_3 .

The assignment of this frequency to the vibrational mode corresponding to ν_3 of a linear molecule is substantiated by such considerations as that the same frequency in the linear isoelectronic molecule, N_2O , is $2232\ \text{cm}^{-1}$. For a symmetrical top, such a parallel vibration should give rise to a line structure on either side of the Q-branch with a spacing of $h/4\pi^2 I_A$ where $I_A = I_B =$ moment of inertia perpendicular to the axis of symmetry. For the structure (a) it would be expected that $I_A = 70 \times 10^{-40}\ \text{g. cm}^2$ approximately. The first attempt to detect this regular structure is shown in Fig. 4. If it is emphasised that each point was determined as the mean of at least four readings, and that the cell transmission was accurately constant over this region, the reality of the series of absorption peaks marked may be considered established. The frequency differences between adjacent members have the values 0.73, 0.98, 0.81, 0.78, 0.50, 0.60, with a mean = $0.73\ \text{cm}^{-1}$: this spacing gives $I_A = 75.8 \times 10^{-40}$. Taking the mean of the first four spacings, as a more reliable estimate, gives

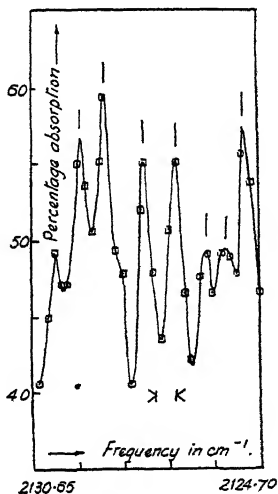


FIG. 4.

⁷ *Z. physik. Chem., B*, 1938, 39, 431.

$I_A = 67 \times 10^{-40}$. These figures provide strong support for the molecular structure favoured. A triangular disposition of the nitrogen atoms would lead to a completely assymmetrical top with moments of inertia of the order $I_A = 48$, $I_B = 30$, $I_C = 18$ in the same units. It was intended to improve this analysis by working with narrower slits and extending the observations to both sides of the central Q-branch, when the work had to be abandoned.

The 8.0 μ Band.

This absorption has been examined only with the fluorite prism, and although it was easy to work with slits of effective width 10 cm^{-1} in this region, this did not suffice to establish unequivocally the type of the band. The frequency of the central peak is 1271 cm^{-1} . Engler and Kohlrausch found a Raman frequency of 1300 cm^{-1} for the liquid, and the identity of these two features may be assumed. On the linear model for the N_3 group in hydrazoic acid, this is assigned to the ν_1 frequency of the group. Accordingly this band should have a structure corresponding to a parallel vibration, which is in agreement with the resemblance of its contour to that of the 4.7 μ band done under low dispersion.

The 8.7 μ Band.

This very intense band extends from 8.4 μ to 9.0 μ , but again the dispersion of the fluorite prism is insufficient to give more than the general

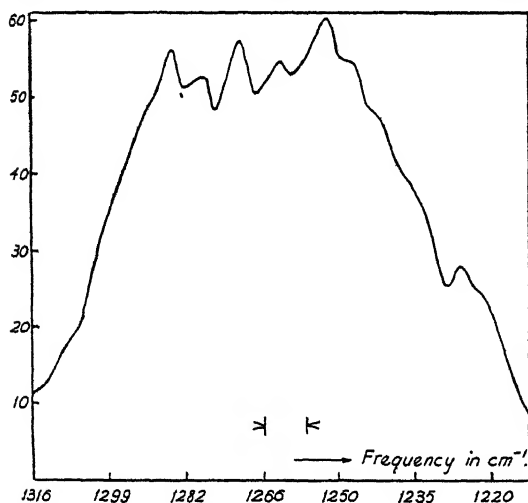


FIG. 5.—The 7.9 μ band.
Path length = 11 cm.
Pressure \approx 6 cm.

form of its contour (see Fig. 6). Provided the foregoing assignments are correct, this absorption must arise from the vibration involving principally the angular deformation of the N—H bond. It is difficult to locate the origin of the band, but the frequency corresponding to 8.7 μ is 1150 cm^{-1} . Actually this is the nearest frequency observed in hydrazoic acid to the well-known deformation frequency in the ammonia molecule at 950 cm^{-1} , and its intensity in the present instance also agrees with this identification.

The 18.5 μ Band.

This absorption is best defined between 17.5 μ and 20.5 μ . Besides the difficulty of recording the small amounts of energy available in this region, the scattering in the spectrometer of small proportions of shorter

wave-length radiations introduces a noticeable impurity in the spectrum. The latter trouble was minimised by working beyond $17.0\ \mu$ with a 5 mm. thick rock-salt shutter : from $11\ \mu$ to $17\ \mu$ a thin fluorite shutter was used. It appears from a comparison with the other results available that the highest frequency which could be given for the centre of this absorption is 555 cm.^{-1} , and the most likely value is 540 cm.^{-1} . A frequency of this

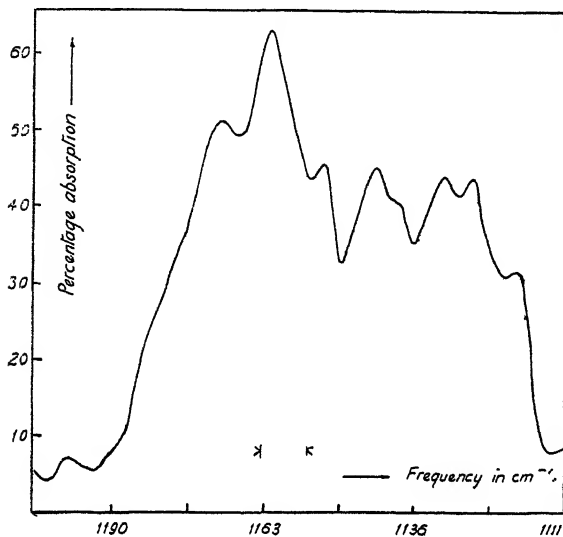


FIG. 6.—The $8.7\ \mu$ band. Path length = 11 cm. Pressure $\approx 3\text{ cm.}$

order is expected for the ν_2 mode of vibration of the linear N_3 group. For the azide ion this frequency* is given as 630 cm.^{-1} .⁸ The peak at 645 cm.^{-1} has been consistently repeated in the absorption measurements, but its intensity is at most one-half of that of the absorption near 550 cm.^{-1} .

This identification completes the assignment of the vibration frequencies in the HN_3 molecule, with the exception of that deformation vibration of

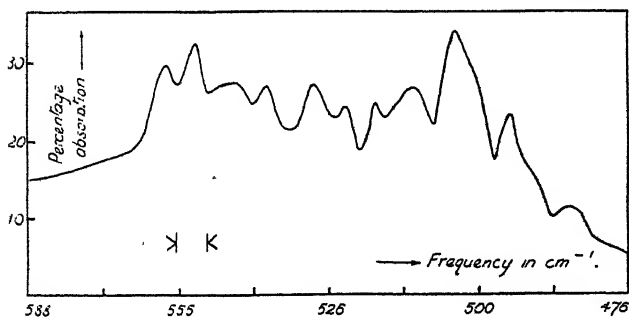
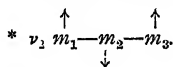


FIG. 7.—The absorption from $17\ \mu$ to $21\ \mu$. 25 cm. cell. 14 cm. pressure.

the N—H bond in which the H atom moves perpendicularly to the plane defined by the N—H and N—N bonds. Three possibilities may be mentioned in this connection : (a) the corresponding frequency may be too small to be included in the range of the present observations ; (b) the $8.7\ \mu$ band may

⁸ Lanseth, Nielsen and Sorensen, *Z. physik. Chem. B*, 1934, 27, 100.



be double, including the origins of both N—H deformation vibrations ;
(c) the weak absorption extending from 13.5μ outwards may be partly due

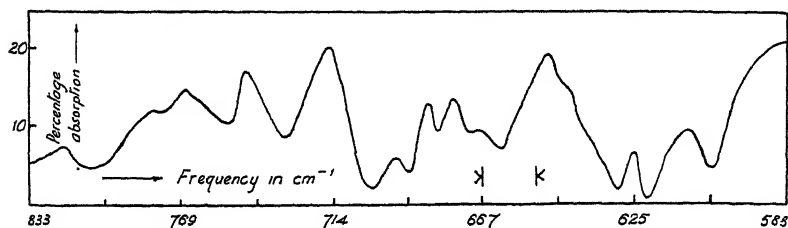


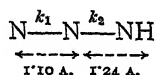
FIG. 8.—The absorption from 12μ to 17μ . 25 cm. cell. 14 cm. pressure.

to the unlocated fundamental. The present data hardly allow of a choice between these alternatives.

General Discussion.

If all these frequencies were accurately determined it would be instructive to analyse completely the different modes of vibration in the model of the HN_3 molecule adduced and to evaluate the constants of a valence-force or other plausible potential function for the structure. Such calculations are obviously superfluous with the present data, and only approximate ones can be presented.

Three of the frequencies have been characterised as involving essentially vibrations within the linear N_3 group, *i.e.* $\nu_1 = 1270 \text{ cm.}^{-1}$, $\nu_2 = 540 \text{ cm.}^{-1}$, $\nu_3 = 2140 \text{ cm.}^{-1}$. These are best related to the molecular model shown,



i.e. $m_1 = m_2 = 14$, $m_3 = 15$. Using the simple equations (9)

$$\nu_1^2 + \nu_3^2 = k_1 \left(\frac{1}{m_1} + \frac{1}{m_2} \right) + k_2 \left(\frac{1}{m_2} + \frac{1}{m_3} \right),$$

and

$$\nu_1^2 \nu_3^2 = k_1 k_2 (m_1 + m_2 + m_3 / m_1 m_2 m_3),$$

the solutions of the quadratics for k_1 and k_2 are found to contain small imaginary terms. This is also the case when the vibrating masses are taken as $m_1 = m_2 = m_3 = 14$, and indicates the necessity for introducing an interaction term into the potential function.⁹ It is readily shown that a cross-term constant k_6 , related to the potential function for linear vibrations $2V = k_1 \Delta_{12}^2 + k_2 \Delta_{23}^2 + k_6 \Delta_{12} \cdot \Delta_{23}$, having the value $k_6 = 1.02 \times 10^5$ dynes/cm. just suffices to make the solutions for k_1 and k_2 completely real and unique: the value so obtained are $k_1 = 13.0$ and $k_2 = 13.5$, in units of 10^5 dynes/cm.

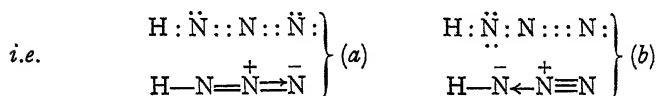
On the practical identity of these force constants, it is permissible to assume a similar identity for the N—N distances in the molecule. With the further assumptions that the N—H distances = 1.01 \AA. (as in NH_3), and the angle $\text{NNH} = 135^\circ$, the value of the moment of inertia $I_A = 67 \times 10^{-40} \text{ g. cm.}^2$ gives the lengths of the N—N bonds as 1.15 \AA. : it is relevant to point out that the limitations in the precise validity of

⁹ Linnett and Thompson, *J.C.S.*, 1937, 1399; *et al.*

the additional assumptions make very little difference to this figure. In the molecular model above, the values adduced by Pauling and Brockway for methyl azide, *viz.* 1.10 Å. and 1.24 Å. are shown. Taking the present estimates, $r_{12} = r_{23} = 1.15$ Å., the force constant k_α governing the angular deformation of the nitrogens is found from $\nu_2 = 540 \text{ cm.}^{-1}$ to be $k_\alpha = 1.07 \times 10^{-11}$ dynes-cm. per radian.

There is a great difference between the above force constants k_1 and k_2 , and the same factors as evaluated by Engler and Kohlrausch, who favour the values $k_1 = 20.37$, $k_2 = 9.12$, in the same units. That this discrepancy arises from the error in their value for ν_3 , is proved by repeating the above calculations using their frequencies. There can be no doubt that the present value for $\nu_3 = 2140 \text{ cm.}^{-1}$ as accurately located and identified for the molecules in the gas phase is very well established. Engler and Kohlrausch's other argument for a considerable difference between the two N—N bonds, depending as it does on the intensities of the Raman lines, is of doubtful significance in the present instance if only for practical reasons.

Application of the octet rule practically limits the electronic structure of the HN_3 molecule to the two possibilities :



and eliminates the structure written by Engler and Kohlrausch,



Whilst remembering their approximate nature, it is significant that the values of the force constants for the N—N bonds are both near the figures characteristic of a double bond: thus, the standard C=C and C=O bonds have the values 9.8 and 12.3×10^5 dynes/cm., respectively,¹⁰ compared with the much higher values of 22.2 and 18.1×10^5 for the triple bonds $\text{N} \equiv \text{N}$ and $\text{C} \equiv \text{N}$. This indicates (a) as the best representation of the molecule.

Brockway and Pauling⁴ have concluded that the electron diffraction results for methyl azide support complete resonance between structures corresponding to (a) and (b). It is initially probable that both these forms should contribute to the normal state of the molecule. Whilst it seems an unavoidable conclusion on the present data that the two N—N bonds are of similar strength to that of a normal double bond, an accurate independent determination of the interatomic distances in the HN_3 molecule would provide further important evidence as to the degree of resonance involved.

The value of $k_\alpha = 1.07 \times 10^{-11}$ dynes-cm./radian is in harmony with those obtained for similar structures, *cf.* Table VII of Sutherland and Penney.¹¹ It is doubtful whether much significance can be attached to the cross-term constant $k_\phi = 1.02 \times 10^5$ dynes/cm., but its sign and magnitude agree with those for like molecules showing a hybrid structure.⁹

¹⁰ Thompson and Linnett, *J.C.S.*, 1937, 1384.

¹¹ Sutherland and Penney, *Proc. Roy. Soc., A*, 1936, 156, 654.

Summary.

An infra-red study of hydrazoic acid, HN_3 , from $2\ \mu$ to $21\ \mu$ has led to the identification of five of its fundamental frequencies: $3336\ \text{cm}^{-1}$, $2139.6\ \text{cm}^{-1}$, $1271\ \text{cm}^{-1}$, $1150\ \text{cm}^{-1}$, and $540\ \text{cm}^{-1}$. The bands at $3336\ \text{cm}^{-1}$ and $2140\ \text{cm}^{-1}$ have been examined under high dispersion. The results indicate a structure in which the N_3 group is linear and an approximate evaluation of their force constants shows that both $\text{N}-\text{N}$ bonds are near normal double bonds.

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THE DEHYDRATION OF SALT HYDRATES BY ENTRAINMENT DISTILLATION WITH LIQUIDS IMMISCIBLE WITH WATER.

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The rates of dehydration of salt hydrates have been measured under widely varying conditions of temperature, pressure, vapour pressure of water, and particle size. Most methods involve observations of the loss in weight during exposure to the chosen conditions; in a second group of methods the hydrate is kept in contact with a liquid miscible with water (*e.g.*, ethyl alcohol, dioxan) and the amount of water lost during dehydration is determined by periodical analysis of the surrounding liquid. A method hitherto not widely explored is provided by the distillation method of estimating water. The application of this method to the examination of a number of salt hydrates has now been investigated.

Methods.

The apparatus used has been fully described in a previous communication.¹ The substance under examination is boiled with a liquid immiscible with and lighter than water, in a flask which is connected to a condenser supported over a calibrated collecting tube. The condensed water and liquid fall into the collecting tube wherein the water remains while the excess of liquid returns automatically to the distillation flask.

Before considering results obtained by this method, it must be noted that the rate of collection of water depends upon two factors, first, the rate of production of water by breakdown of the salt hydrate, and second, the rate at which this liberated water is conveyed from the flask to the collecting tube. Provided the latter rate is as great as, or greater than, the former, it is assumed that the rate of collection of water in the collecting tube will be a measure of the rate of release of water from the salt

¹ Tate and Warren, *Analyst*, 1936, 61, 367.

hydrate. Experiment has shown that this transfer of water is effected in a relatively short time when using liquids with a B.P. over 80° C. The measured rates of collection are best indicated on a curve by plotting volume collected against time. The accuracy of this curve is dependent on the frequency of readings, and to obtain the highest accuracy the volume collected is measured after the arrival of each drop of water in the receiving tube, the time being noted simultaneously.

When using liquids boiling below 80° C. the rate of transference of water by the entraining liquid becomes too slow to be practicable, while above 160° the water drop on the end of the condenser tends to boil and splutter rather than drop cleanly into the measuring tube. The application of the method is therefore limited to a temperature range of 80° - 160° C.

Discussion.

The curves obtained by plotting "water collected" against "time" were found to fall into three groups.

1. Dehydration proceeded smoothly from the initial to the end product, the rate either remaining approximately constant till the final product had been formed or falling steadily with no sudden variations and becoming zero when the composition of the dehydrating mass had become that of the end product.

2. Dehydration proceeded smoothly at a constant or gradually decreasing rate until the dehydrating mass had attained a certain composition. At this point, the rate of dehydration suddenly diminished, the curve, therefore, showing a discontinuity or "break."

3. As with the second group, dehydration proceeded smoothly to a certain point, at which a sudden increase in rate of dehydration occurred. A discontinuity or "break" was again apparent in the curve at this point.

Curves of type 1 are afforded by a large number of salt hydrates. Such a curve can be produced by a hydrate decomposing directly into the end product and water, as well as by a salt hydrate decomposing into a lower hydrate which in turn rapidly decomposes into the end product. From curves of this type, it is difficult to draw conclusions respecting the structure of the dehydrating mass, particularly as to the formation of possible intermediate hydrates. The only definite entities are the initial and end products.

The second type of curve has frequently been encountered in previous work. The rate of dehydration of barium chloride dihydrate was found by T. W. Richards² to change suddenly at a point corresponding to the monohydrate. During the dehydration of copper sulphate pentahydrate Rae³ and Garner and Tanner⁴ observed a similar "point of inflexion" or "change in direction" at the point corresponding to the trihydrate. Hackspiel and Kieffer⁵ found similar curves with various salts. The changes in direction observed by these investigators were in every case found to occur when the composition of the dehydrating mass closely approximated to an intermediate hydrate, and were correlated with the formation of the hydrate. Garner and Tanner obtained further justification for this by a microscopic examination which revealed that the trihydrate of copper sulphate was in fact formed.

It is now accepted that a discontinuity in the rate of dehydration of a salt hydrate indicates the formation of an intermediate hydrate.

² *Z. anal. Chem.*, 1898, **37**, 583.

⁴ *Ibid.*, 1930, 47.

³ *J.C.S.*, 1916, 1229.

⁵ *Ann. Chim.*, (10), 1930, **14**, 227.

Crowther and Coutts⁶ summarised this view in the words "the existence of sudden changes in the rate of dehydration has been used as evidence of the existence of definite hydrates, even in cases where the hydrate concerned has not been isolated." A discontinuity observed in the rate of dehydration by distillation with boiling liquids can, therefore, reasonably be ascribed to the formation of a hydrate of composition corresponding to the dehydrating mass at the time of the break.

Curves of the third type are less frequently encountered than the other two. Good examples were provided by the work of Crowther and Coutts⁶ and of Hume and Colvin.⁷ The former workers observed a break during the dehydration of copper sulphate pentahydrate under certain conditions. This break was a short pause, of a few minutes' duration, in the loss of water, and it occurred when the dehydrating mass had the composition of the trihydrate. A similar break occurred at the composition of the monohydrate when more intense dehydrating conditions were used. Very similar dehydration curves were provided by barium chloride dihydrate, the breaks being of considerably longer duration. Hume and Colvin studied the dehydration of copper sulphate pentahydrate *in vacuo*, and obtained a well marked "point of inflexion" at the composition of the trihydrate. Their dehydration curves are similar to those included by us in type 3. Both groups of workers associated the discontinuity in the rate of dehydration with the formation of an intermediate hydrate.

It appears, therefore, to be the well established practice to ascribe discontinuities such as those observed in curves of the second and third type to the formation of hydrates. On this basis our curves of the second type provide evidence for the formation of copper sulphate monohydrate (160° C.); magnesium sulphate trihydrate (80°, 100°, 110°) and dihydrate (110°, 120°); ferrous ammonium sulphate dihydrate (100°, 110°, 120°) and nickelous sulphate tetrahydrate (100°, 110°, 120°). Curves of the third type provide evidence for the formation of ferrous sulphate tetrahydrate (80°); zinc sulphate tetrahydrate (80°) and nickelous sulphate hexahydrate (80°). The end products of the dehydration of salts yielding curves of the first type are copper sulphate monohydrate (80°, 100°); magnesium sulphate monohydrate (160°); ferrous sulphate monohydrate (80°, 100°); ferrous ammonium sulphate dihydrate (80°); zinc sulphate monohydrate (80°, 100°, 120°); nickelous sulphate tetrahydrate (80°) and manganous sulphate monohydrate (80°, 100°, 120°).

It is to be remarked that although a discontinuity in a dehydration curve may be evidence for the formation of a hydrate, the absence of such a discontinuity is not to be taken to indicate that intermediate hydrates are not formed during the distillation under consideration. As already pointed out, the first type of curve can accord with the formation of lower hydrates although no discontinuity is observed. Moreover, from the limitation in the temperature range of distilling liquids, it is not to be expected that all hydrates observable by other means could be detected by the distillation method. Similar limitations apply to other methods. For example, the study of the dehydration of the common hydrates of the sulphates of magnesium, nickel, cobalt, zinc, and the chlorides of strontium, magnesium and cobalt, using a continuous reading balance (Crowther and Coutts)⁶ did not reveal the forma-

⁶ *Proc. Roy. Soc., A*, 1924, 106, 215.

⁷ *Ibid.*, 1931, 132, 548.

tion of lower hydrates, although many are known. It is at present difficult to interpret the phenomena observed with salts which melt under the distillation liquid but attention is now being devoted to this problem.

Particular interest attaches to several of the lower hydrates observed above. The only evidence previously advanced for the existence of magnesium sulphate trihydrate was provided by J. B. Hannay⁸ from data concerning the rate of dehydration of the heptahydrate in hot air. We have failed to reproduce Hannay's experimental findings, but now advance the evidence obtained by distillation for the existence of the trihydrate (Fig. 1). No reference has been found in the literature to the dihydrate of ferrous ammonium sulphate, which appears to be formed when the hexahydrate is distilled with liquids boiling at temperatures between 80° and 120° (Fig. 3). It is remarkable that, whereas dehydration of nickel sulphate heptahydrate in air proceeds rapidly to the dihydrate, dehydration under boiling liquids proceeds first to the tetrahydrate which then decomposes comparatively slowly (Fig. 2). From the literature, the tetrahydrate of nickel sulphate appears difficult of access (it has been reported as an unstable salt which decomposes slowly), but it appears to be formed readily when the heptahydrate is distilled with cyclohexane. The stability of the tetrahydrate has been stated to be comparable with that of the pentahydrate, of which no trace has been found by the distillation method (Fig. 2). The evidence for the existence of zinc sulphate tetrahydrate (Fig. 3) is of particular interest, as this hydrate has hitherto been detected only under exceptional conditions.⁹

Experimental.

Copper Sulphate Pentahydrate.

The tri- and monohydrates are well defined; the existence of the dihydrate has been reported but is more doubtful.

Dehydration in Oven. The sample used lost 28.4 per cent. of its weight when heated for 1 hr. at 100° C. (theoretical for loss of 4 mol. water is 28.8 per cent.). No further loss occurred on prolonged heating.

Distillation.—1. **Benzene** B.P. 80° C. Lost 4 mol. water (27.4 per cent.) after 3 hr.

2. **Cyclohexane** B.P. 80° C. Lost 4 mol. water (28.3 per cent. in 5 hr.; no further loss after further 5 hr.).

3. **Light Petroleum** B.P. 80° C. Lost 4 mol. water (28.1 per cent. in 2 hr.; no further loss after further 2 hr.).

4. **Heptane** B.P. 100° C. Lost 4 mol. water (28.3 per cent. in 1 hr.; no further loss after further 4 hr.).

With the above four liquids the rate diminished steadily, becoming zero after loss of 4 mol. water. There was no discontinuity after the loss of 2 mol. water. All curves were of type 1.

5. **Light Petroleum** B.P. 160° C. 28 per cent. was lost very quickly (20 min.). The rate of loss diminished greatly after about $3\frac{1}{2}$ mol. water had been lost, becoming about 1/600 of its original value. After 18 hr., the total loss was 33.6 per cent. (theoretical for loss of 5 mol. water is 36.0 per cent.). Curve type 2.

Manganous Sulphate Tetrahydrate.

The existence of the tri-, di- and monohydrates has been reported. There is some doubt concerning the tri- and dihydrates.

⁸ J.C.S., 1877, 381.

⁹ P. Vallet and M. Bassiere, *Bull. Soc. Chim.*, 1938, 5, 546.

Dehydration in Oven. The sample used lost 25.2 per cent. by weight when heated at 90° C. for 30 min. A further 0.3 per cent. was lost during 3 hr. (theoretical for loss of 3 mol. water is 24.3).

Distillation.—1. **Cyclohexane** B.P. 80° C. Lost 25.2 per cent. in 25 min. and 25.4 per cent. in 4 hr. Curve type 1.

2. **Heptane** B.P. 100° C. Lost 25.1 per cent. in 20 min. and 25.6 per cent. in 4 hr. Curve type 1.

3. **Light Petroleum** B.P. 120° C. Lost 25.1 per cent. in 11 min., and 25.7 per cent. in 4 hr. Curve type 1.

With each of the above liquids there was a rapid loss of 3 mols. water (theoretical 24.3 per cent.). Dehydration proceeded no further.

Ferrous Ammonium Sulphate Hexahydrate.

The hexahydrate is the only hydrate reported.¹⁰

Dehydration in Oven. The sample used lost 18.7 per cent. after 2 hr. and underwent no further loss during 17 hr. (theoretical for loss of 4 mol. water is 18.4 per cent.).

Distillation.—1. **Cyclohexane** B.P. 80° C. Water was lost at a gradually decreasing rate. At the end of 2 hr. 17.2 per cent. loss had occurred; after 4½ hr. 18.5 per cent. loss, with no further loss during a further 5 hr. (theoretical for loss of 4 mol. water is 18.4 per cent.). Curve type 1.

2. **Heptane** B.P. 100° C. Results similar to cyclohexane. Lost 18.8 per cent. in 2 hr.; 18.9 per cent. in 4 hr., then constant. Curve type 1.

3. **Light Petroleum** B.P. 110° C. (Fig. 3). 18.6 per cent. was lost rapidly (40 min.). The rate then diminished abruptly to 1/10 of its previous value. The rate slowly decreased; during 7 hr. there was eliminated a total of 24.3 per cent. (5.3 mol.). There was no change in rate at the loss of 5 mol. water (23 per cent.). Curve type 2.

4. **Light Petroleum** B.P. 120° C. After a rapid initial loss of 4 mol. water (17.0 per cent. in 10 min.) dehydration slowed abruptly to 1/3 of its previous value. After 6 hr. there was a total loss of 24.7 per cent. (5.4 mol.) again no change in rate being observed at the loss of 5 mol. water. Curve type 2.

Magnesium Sulphate Heptahydrate.

The existence of the mono-, di-, hexa- and heptahydrates seems well established. Hydrates containing 1½, 3 and 5 mol. water have been reported, but their existence is uncertain.

Dehydration in Oven. The material used lost 36.3 per cent. rapidly, leaving the dihydrate (theoretical for loss of 5 mol. water is 36.5 per cent.). The residual dihydrate decomposed very slowly, leaving after 100 hr. a residue approximating in composition to the monohydrate (total loss 42.2 per cent.; theoretical for loss of 6 mol. water is 43.8 per cent.). There was no discontinuity at the loss of 4 mol. water.

Distillation.—(Fig. 1). 1. **Benzene** B.P. 80° C. 29.6 per cent. was lost in 80 min. leaving the trihydrate (theoretical for loss of 4 mol. water is 29.2 per cent.). The rate diminished after the loss of 3½ mol., becoming constant at about 1/30 the previous value. After 4 hr. 40 min. the total loss was 4.51 mol. Curve type 2.

2. **Heptane** B.P. 100° C. After the loss of 3½ mol. water the rate of dehydration diminished, becoming about 1/70 after loss of 4 mol. Decomposition proceeded at a diminishing rate; after 22 hr. there was a total loss of 40.4 per cent. (5.5 mol.). Curve type 2.

3. **Light Petroleum** B.P. 110° C. As with heptane, the rate diminished during the loss of 3½ to 4 mol., becoming about 1/40 the previous

¹⁰ References to dehydration of the hexahydrate, e.g., H. A. von Vogel, *J. prak. Chem.*, 1834, 1, 2, 192; and T. Shibita and M. Fukushima, *Bull. Chem. Soc. Japan*, 1928, 3, 118, do not give the composition of the dehydration product.

value. Decomposition continued at this new constant rate for 4 hr. while a further mol. of water was eliminated (loss 37.2 per cent.; theoretical for loss of 5 mol. water is 36.5 per cent.). The rate then diminished abruptly to about $\frac{1}{3}$ of the previous value, and became too slow to permit following completely to the monohydrate. (38.4 per cent. loss after 7 hr.; theoretical for loss of 6 mol. water is 43.8 per cent.). Curve type 2.

4. **Toluene**. B.P. 110° C. The course of decomposition was similar to that with light petroleum B.P. 110° C. 4 mol. water were lost rapidly. (28.2 per cent. after 15 min., 29.6 per cent. 30 min.). The rate then diminished, becoming constant at about $\frac{1}{35}$ of its original value. One further mol. water was eliminated at this rate during 3 hr. (total loss 36.7 per cent.; theoretical for loss of 5 mol. water is 36.5 per cent.). The rate then again diminished to about $\frac{1}{3}$ the previous value, becoming too slow to follow decomposition completely to the monohydrate (38.2 per cent. loss after $5\frac{1}{2}$ hr.). Curve type 2.

5. **Light Petroleum** B.P. 120° C. Five mol. water were lost in 35 min. (34.8 per cent.; theoretical 36.5 per cent.). There was indication of a slackening in rate after loss of the first 4 mol. water, but the difference

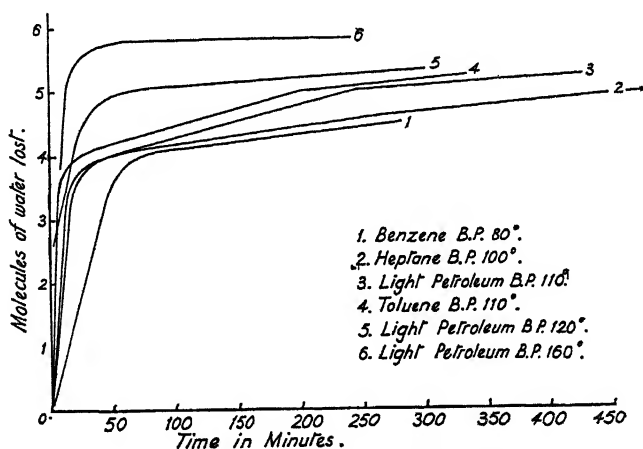


FIG. 1. Dehydration of magnesium sulphate heptahydrate.

Continuation of above observations:—Lost 5.5 mols. water in 22 hours under heptane.

in rates before and after this point were not so marked as with the liquids described above. The rate of decomposition became very slow after loss of 5 mol. water (total loss after $1\frac{1}{2}$ hr. 37.0 per cent.; after 5 hr. 39.0 per cent.). Curve type 2.

6. **Light Petroleum** B.P. 160° C. Six mol. water were lost rapidly (40.4 per cent. in 25 min.; 42.0 per cent. in 60 min.; theoretical for loss of 6 mol. water is 43.8 per cent.). The rate then diminished almost to zero, a further 0.6 per cent. being lost in 4 hr. Curve type 1.

Nickel Sulphate Heptahydrate.

All hydrates up to the heptahydrate have been reported.¹¹ The hepta-, hexa- and monohydrates appear to be best established.¹²

Dehydration in Oven. When heated at 80° or 100° the heptahydrate lost 5 mol. water (31.3 per cent.; theoretical for 5 mol. water is

¹¹ Chretien and Rohmer, *Compt. Rend.*, 1934, 198, 92.

¹² I. N. Plaskin, *C.A.*, 1936, 8060; *Ann. secteur anal. phys.-chim.*, *Inst. chim. gen.* (U.S.S.R.), 1936, 9, 271.

32.1 per cent.) in about 15 hr. A further small loss of 0.1 per cent. occurred during the next 17 hr. and the weight was then unchanged after a further heating for 17 hr. On resuming heating at 120° C. further small losses occurred; after 17 hr. the total loss was 32.3 per cent., after 34 hr. 34.6 per cent.

Distillation.—(Fig. 2). 1. Cyclohexane B.P. 80° C. During the first hour water was lost at a steady rate, 1 mol. being removed (7.5 per cent.; theoretical for loss of 1 mol. is 6.4 per cent.). The rate of loss of water then increased to approximately twice its previous value, and after continuing at this higher rate for an hour, diminished almost to zero after the total loss of 3 mol. water in 3 hr. (19.0 per cent.; theoretical for loss of 3 mol. water is 19.2 per cent.). After 9½ hr. there was a total loss of 19.4 per cent. (3.03 mol.). Curve type 3.

It was found that admixture with sand caused a great increase in the rate of loss of the first molecule of water. In 15 min. a loss of 6.2 per cent. was recorded after which the rate fell to about 1/9th and remained

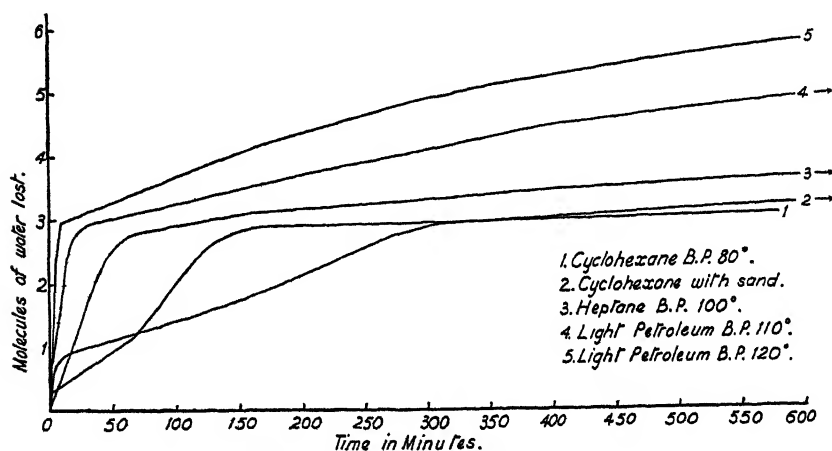


FIG. 2 Dehydration of nickel sulphate heptahydrate.

Continuation of above observations :—2. 3.87 mols. water lost in 11 hours.
3. 4.43 mols. water lost in 24 hours.
4. 5.46 mols. water lost in 23 hours.

constant during the next 5 hr., at the end of which time 18.9 per cent. water had been lost. The rate then decreased again to 1/9th, the loss after 11 hr. being 24.8 per cent. Curve types 3 and 2.

2. Heptane B.P. 100° C. Three mol. water were lost in 2 hr. The rate diminished to about 1/40th the previous value after the loss of 2½ mol. water; after 5½ hr. 21.6 per cent. (3.37 mol.) had been lost, and after 24 hr. 28.4 per cent. (4.43 mol.). Admixture with sand had no effect upon the course of decomposition. Curve type 2.

3. Light Petroleum B.P. 110° C. Three mol. water (19.0 per cent.) were lost very rapidly (50 min.). The rate diminished to about 1/34th after the loss of 2½ mol. and a total loss of 35 per cent. (5.46 mol.) was recorded during 23 hr. There was no indication of the formation of intermediate hydrates. Curve type 2.

4. Light Petroleum B.P. 120° C. After a rapid initial loss of 3 mol. water (19.2 per cent. in 15 min.) the rate of decomposition fell to about 1/50th the previous value. After 10 hr. there was a total loss of 37 per cent. (5.77 mol.) and decomposition had become too slow to permit following further. Curve type 2.

Zinc Sulphate Heptahydrate.

The hexa- and monohydrates have been clearly established. The penta-, tetra-, di- and an intermediate hydrate containing $3\frac{1}{2}$ mol. water have been reported, but evidence for their individuality is indecisive.

Dehydration in Oven. The sample used lost 36.0 per cent. in 1 hr. (theoretical loss for 6 mol water is 37.6 per cent.). Dehydration continued at a very slow rate on further heating.

Distillation.—1. Cyclohexane B.P. 80° C. (Fig. 3). 18.4 per cent. was lost at a uniform rate in 39 min. (theoretical for loss of 3 mol. water is 18.8 per cent.). The rate then suddenly increased to about 5 times its previous value and a further 3 mol. water were lost (36.6 per cent. in 51 min.; theoretical for loss of 6 mol. is 37.6 per cent.). The rate of dehydration then fell to zero. Curve types 3 and 1.

2. Heptane B.P. 100° C. Decomposition proceeded much more rapidly than with cyclohexane. Some experiments indicated a slight increase in rate at the composition of the trihydrate, but in most cases

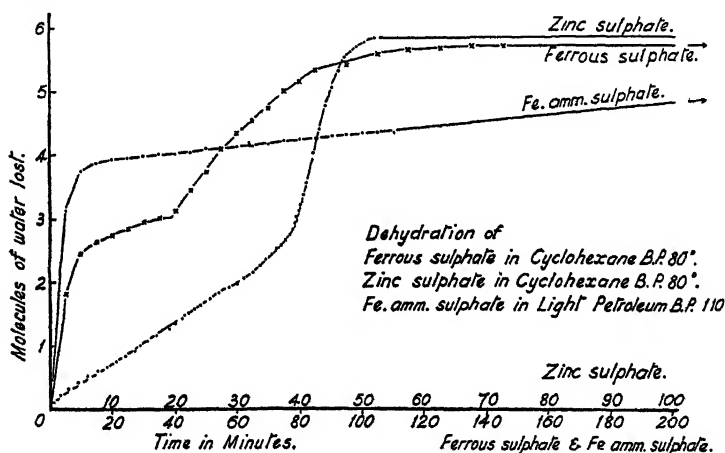


FIG. 3.

Continuation of above observations :—Ferrous sulphate lost 5.7 mols. water in 7 hours.

Fe. amm. sulphate lost 5.3 mols. water in 7 hours

the speed of dehydration was too great to permit detection of the trihydrate. Six mol. water were eliminated in 17 min. (37.0 per cent.; theoretical loss for 6 mol. is 37.6 per cent.). There was no further loss during the next two hours. Curve type 1.

3. Light Petroleum B.P. 110° C. Six mol. water (36.5 per cent.) were lost in 15 min. There was no further loss after $1\frac{1}{2}$ hr. Curve type 1.

Ferrous Sulphate Heptahydrate.

The di- and monohydrates of ferrous sulphate are well defined. Hydrates containing 6, 5, 4 and 3 mol. water have been reported; their individuality is not so well defined.

Dehydration in Oven. The sample used lost 37.4 per cent. of its weight when heated for 17 hr. at 100° C. (theoretical for loss of 6 mol. water is 38.8 per cent.).

Distillation.—1. Cyclohexane B.P. 80° C. (Fig. 3). There was a rapid initial loss of 19.6 per cent. in 38 min. (theoretical for loss of 3 mol. water is 19.4 per cent.), the rate becoming less in the later stages. The

rate suddenly increased to 3 times its previous value after 3 mol. water had been lost, then slowly decreased, becoming zero after total loss of 37.8 per cent. (theoretical for loss of 6 mol. water is 38.8 per cent.) during 140 min. There was no further loss during 5 hr. Curve types 3 and 1.

2. **Heptane** B.P. 100° C. Rapid loss of 37.2 per cent. in 50 min. (theoretical for loss of 6 mol. water is 38.8 per cent.). Rate then diminished almost to zero (total loss after 5 hr. was 37.4 per cent.). Curve type 1.

Summary.

The investigation of the rate of dehydration of salt hydrates when distilled under liquids immiscible with water, and the limitations of the method, are discussed. Dehydration curves of seven salt hydrates have been obtained and found to be similar in character to those obtained by other methods. Evidence has thereby been obtained for the existence of several otherwise ill-defined hydrates. The work will be extended to include the examination of other salt hydrates of a type different from the sulphates described in this communication.

The authors wish to acknowledge the assistance of Mr. G. A. C. Ashcroft, B.Sc., in the experimental work involved in this investigation, and to thank the Government Chemist, Dr. J. J. Fox, C.B., O.B.E., F.I.C., for his interest in this work and his permission to publish the data so far recorded.

A STUDY OF FILMS AT THE LIQUID/LIQUID INTERFACE.

Part III.—A Specific Effect of Calcium Ions on Kephalin Monolayers.

By A. E. ALEXANDER,* TORSTEN TEORELL and C. G. ÅBORG.

Received 10th July, 1939.

The peculiar permeability properties displayed by living cells have for long been attributed to the presence of a special membrane surrounding them.¹ It is now generally accepted that these cell membranes are constituted of lipoids and proteins, the thickness being of the order of a few molecular layers.² These constituent molecules, at least those in the outermost layers which primarily determine the membrane characteristics, are supposed to be regularly orientated as in interfacial monolayers prepared artificially.³ Hence it would appear profitable to study the action of various reagents upon model monolayers of the constituents of actual cell membranes in order to see if there is any correlation with their known biological effects. Some promising investigations along

* Rockefeller Foundation Fellow, 1939-40.

¹ See, for instance, L. V. Heilbrunn, *Outlines of General Physiology*, Philadelphia and London, 1937, p. 82.

² H. Fricke, *J. gen. Physiol.*, 1925, 9, 137; *Cold Spring Harbor Symposia on Quantitative Biology*, 1933, 1, 117. J. F. Danielli, *J. gen. Physiol.*, 1935, 19, 19.

³ J. F. Danielli and H. Davson, *J. Cell. and Comp. Physiol.*, 1935, 5, 495. J. F. Danielli, *ibid.*, 1936, 7, 393.

these lines have already been carried out.⁴ So far model experiments on monolayers have been confined to the air/water interface, but using a new technique recently described⁵ these can now be extended to the oil/water interface. We believe that such oil/water interfacial films simulate more closely the actual biological conditions.

This paper is concerned chiefly with the behaviour of salts

(NaCl, KCl, MgCl₂ and CaCl₂)

towards kephalin, one of the chief members of the phosphatide group of cell lipoids, when spread as a monolayer at the air/water and benzene/water interfaces. That there might be some differential activity towards phospho-lipoids had been suggested by some of our earlier observations on lecithin films at the benzene/water interface, where a certain stabilising action of calcium ions had been noted. With kephalin monolayers, particularly at the latter interface, a much more pronounced, and apparently "specific" effect of calcium ions has been found. The possible biological significance of this finding is discussed later, but it can be emphasized that, of the various inorganic ions which affect cell and organ functions, calcium seems to play a rôle of first importance, being necessary, for instance, for the integrity of cell membranes, for normal irritability of the nervous apparatus and for blood clotting.⁶

Experimental Method.

The tensions at the benzene/water interface were determined using the du Noüy Interfacial tensiometer manufactured by the Central Scientific Co., U.S.A. It was necessary to use a platinum-iridium ring owing to the ease with which one of copper lost its wetting properties when in contact with a kephalin film. Full details of the method for insoluble interfacial films have recently been published.⁵ For spreading purposes the kephalin, a highly purified specimen prepared by Professor Blix in this laboratory by the method of Wadsworth, Maltaner and Maltaner,⁷ was dissolved in 60 per cent. isopropyl alcohol.

Monolayers at the air/water interface were examined by the usual methods of surface pressures and surface potentials,⁸ the kephalin being spread from a petrol-ether solution.

Experimental Results.

The various types of curve given by kephalin when using different aqueous substrates are shown in Fig. 1. In accordance with the usual practice they are expressed as the variation of the interfacial tension lowering (F) in dynes/cm., as a function of the area per molecule (A) in Å². The substrates used have been distilled water, M/200 CaCl₂, M/10 NaCl, M/10 KCl, M/200 MgCl₂, N/10 HCl and N/10 NaOH. With the exception of the last two the substrate pH lay between 5 and 6, and was controlled colorimetrically before and after the experiment to see if any significant shift had occurred. The redistilled water from a Jena glass still was freshly collected before use in a "Pyrex" flask to reduce the calcium contamination to a minimum.

⁴ J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., B*, 1937, **122**, 29; *Nature*, 1939, **144**, 100.

⁵ A. E. Alexander and T. Teorell, *Trans. Faraday Soc.*, 1939, **35**, 727.

⁶ See, for instance, ¹, pp. 370-374.

⁷ A. Wadsworth, F. Maltaner and E. Maltaner, *Amer. J. Physiology*, 1931, **97**, 74.

⁸ N. K. Adam, *The Physics and Chemistry of Surfaces*, Oxford, 1938, p. 17.

It can be seen from Fig. 1 that the curves fall sharply into two classes, the first including the calcium chloride and hydrochloric acid substrates, the second all the other substrates examined. The former gave reproducible curves which were identical within the experimental error, whereas the latter showed a progressive shift to smaller areas as the time taken for the measurements was increased. The discrepancy between the two types is also seen to increase with increasing values of F .

In Fig. 1 is also shown the effect of injecting calcium chloride into the substrate (giving a concentration of $M/200$) after a certain amount of kephalin had been spread.

Some experiments were also carried out using a solution of kephalin in the benzene phase to examine the effect of calcium ions in the aqueous phase on the interfacial tension. The method was to commence with pure benzene and the desired aqueous substrate ($M/200$ CaCl_2 and redistilled water were used) and after determining the initial interfacial tension to

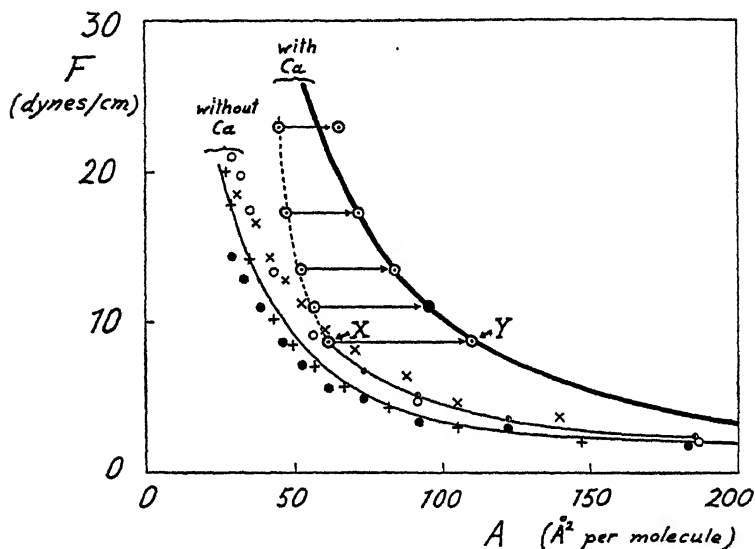


FIG. 1.— F - A curves for kephalin at the $\text{C}_6\text{H}_6/\text{H}_2\text{O}$ interface in the presence of various ions. (—) $M/200$ CaCl_2 and $N/10$ HCl ; (---) distilled water; (○---○) distilled water and addition of CaCl_2 at point X; (●) $N/10$ NaCl ; (●) $N/10$ KCl ; (+) $M/200$ MgCl_2 ; (x) $N/10$ NaOH .

add small amounts of a solution of kephalin in benzene. The benzene solution was stirred for a definite time (generally one minute) and the interfacial tension redetermined. While it must be emphasised that the values so obtained are not equilibrium ones, yet the experiment showed that for a given kephalin concentration the I.T. lowering was invariably greater when calcium ions were present.

Finally, the effect of calcium ions was examined on a kephalin film at an air/water interface. Films were spread on various substrates ($N/100$ HCl , distilled water, and buffers of pH 7.4 and 9.2) and the force-area and potential-area curves compared in presence and absence of $N/10$ NaCl and $M/100$ CaCl_2 . Neither of these salts appeared to have any very marked effect, although with the calcium chloride there was an increase in potential of ca 30-40 mV and a slight contraction of the film. The film was of the liquid-expanded type and closely resembled that of lecithin in its limiting area (104 as compared with 116 \AA^2),⁹ but with a much lower apparent

⁹ A. H. Hughes, *Biochem J.*, 1935, 29, 430.

dipole moment (ca 470 MD compared with ca 740⁹ at 100 Å²/mol., p_H 7.4.) [1 MD = 10⁻²¹ e.s.u.].

Discussion of Results.

It would seem that although surface films of kephalin at the air/water interface are little affected by the nature of the ions present in the substrate, yet at the benzene/water interface a marked, and apparently specific effect, is brought about by calcium ions. This appears to be due to an "anchoring" of the kephalin molecules to the interface by the calcium ions which thus prevents their dissolution into the benzene phase.

That this is the correct explanation is supported by the above experimental results, which can be summarised as follows:—

(a) When using substrates of distilled water, sodium hydroxide, and sodium, potassium or magnesium chlorides, the F - A curves were very

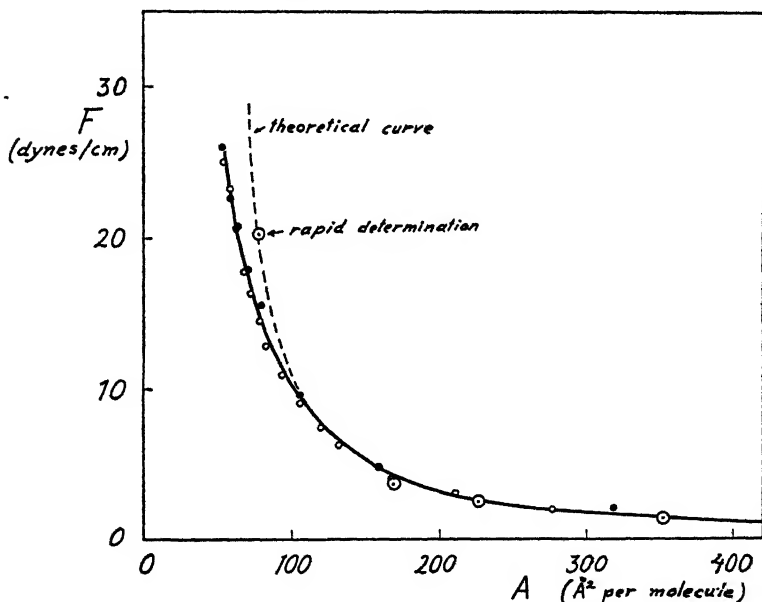


FIG. 2.— F - A curve for kephalin on a substrate containing Ca-ions. The dotted curve is calculated from the equation $(F - 0.7)(A - 49.5) = 593$.

much more dependent upon the time factor than when calcium ions were present, and the "minimum" areas calculated (A_0) were often less than 40 Å², which is the smallest permissible area for the two hydrocarbon chains in the kephalin molecule.

(b) The F - A curve given on the calcium chloride substrate was found to obey the hyperbolic van der Waals' equation

$$(F - F_0)(A - A_0) = C,$$

exactly as previously shown for other *insoluble* films at the benzene/water interface.⁵ There is a slight discrepancy between the theoretical and experimental values at high values of F (i.e. at low interfacial tensions), indicating a slight solubility above ca 10 dynes (see Fig. 2), but evidently

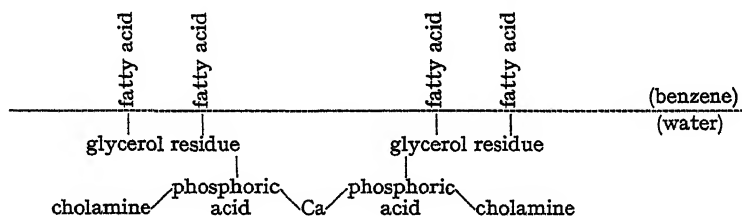
the kephalin film has been anchored comparatively firmly. Incidentally the values of F_0 , A_0 and C in the above equation are 0.7, 49.5 and 593 respectively, which are of the order expected by analogy with the results for lecithin.⁵

(c) If CaCl_2 is added in the middle of an experiment using, say, distilled water, then the subsequent injections of kephalin can be shown to remain in the interface. A typical such run is shown in Fig. 1, calcium chloride being added at the point X. Assuming that the interfacial concentration is then given by the point Y, then the points given by subsequent additions of kephalin are shown by the circles indicated. These lie so closely on the usual calcium chloride curve that evidently all the kephalin spread after the point X has remained in the interface.

(d) Finally, as mentioned above, there is the fact that the capillary activity of a benzene solution of kephalin is greater when calcium ions are present in the aqueous substrate.

On air/water films we obviously cannot expect to find calcium effects like those demonstrated above, but that a reaction occurs is indicated by the potential changes which have been mentioned previously.

The effect of calcium ions is probably due to the formation of an *insoluble** calcium salt through the phosphoric acid groups of two molecules of kephalin, this decrease in solubility and doubling of the size of the molecule stabilising it in the interface. A schematical structure for this compound as present in the interface would be



This is supported by the findings of Wadsworth, Maltaner and Maltaner,⁷ and of Stenhagen,¹⁰ that kephalin emulsions in the presence of calcium chloride form an insoluble calcium di-kephalin salt with liberation of hydrochloric acid (Stenhagen¹⁰ showed that the pH of a neutral suspension could be lowered to 3 by this means). In the interfacial monolayer, which is the seat of reaction in emulsions, we can envisage this reaction producing, at any rate temporarily, a high local hydrogen ion concentration.

The fact that $N/10$ HCl can also act as an "anchor" for the kephalin molecule at the benzene/water interface is not so readily explicable as is that of calcium ions. For a molecule to remain at such an interface it seems from our previous work that rather a nice balance is necessary between the polar and non-polar portions of the molecule, lecithin being the best example of such a balance found so far. With lysolecithin and sodium cetyl sulphate the polar part predominates and confers some water solubility, whereas kephalin shows appreciable *benzene* solubility. Hence at first sight it would appear that the strongly acid substrate stabilises the kephalin molecule in the interface by increasing the hydrophilic nature of the polar group by salt formation. If this is the

* Insoluble in both phases.

¹⁰ E. Stenhagen, *Skand. Arch. Physiol.*, 1937, 77, 77.

correct explanation, however, it is a little difficult to understand why strong alkali does not show a similar stabilisation, owing to the amphoteric nature of the kephalin molecule.††

As to the possible biological implications of these calcium effects it does not seem profitable to speculate a great deal at present. Danielli and Davson³ have suggested that the replacement of sodium by calcium might result in a decreased water permeability, owing to the lower water affinity of calcium-lipoid compounds. Besides this mechanism one might suggest another possibility. The usual cell membranes are probably a few molecular layers thick, and so one can picture the calcium ions "pulling" kephalin molecules into the interface, resulting in an increased molecular packing and a lowered interfacial tension. The thus "tightened" membrane would be expected to show a generally decreased permeability.

Summary

(1) In view of the possible biological significance the effect of various cations on monolayers of kephalin at the benzene/water and air/water interfaces has been examined.

(2) At the air/water interface there was little marked effect, although calcium ions caused a slight condensation of the film and an increase of some 30-40 mV in the surface potential.

(3) At the benzene/water interface calcium ions showed a specific effect, which was not given by either sodium, potassium or magnesium ions, although a similar effect was obtained on strongly acid and alkaline substrates (*e.g.* N/10 HCl and N.NaOH).

(4) This effect has been shown to be a stabilization of the kephalin in the interface, preventing its dissolution into the benzene phase.

(5) The cause of the stabilizing action of calcium ions and some possible biological inferences are discussed.

The expenses of this investigation were defrayed by the Rockefeller Foundation and the Therese and Johan Andersson Foundation.

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The University of Uppsala,
Sweden.*

†† We have since found that very strongly alkaline substrates (*e.g.* N. NaOH) bring about a stabilisation equal to that of N/10 HCl, which removes this apparent anomaly.

THE VAPOUR PRESSURE CURVE OF LIQUID HELIUM BELOW THE λ -POINT.

BY B. BLEANEY AND F. SIMON.

Received 24th July, 1939.

There are two main reasons for the importance of an accurate knowledge of the vapour pressure curve of helium: (*a*) the *p-T* correlation is the chief means of determining temperatures in the liquid helium region, and is therefore of great practical value. This is especially true of the lowest region down to 1° K., which is essential for the calibration of the susceptibility of paramagnetic salts used in the magnetic

cooling method. (b) The rational vapour pressure formula will supply information concerning the difference between the entropy of liquid and gas.

The case of helium is exceptional in so far as it is difficult to obtain reliable experimental data at the lowest temperatures. This is due to the fact that up to the present only gas thermometers have been used for the determination of the temperature. Obviously at low values of the vapour pressure still lower pressures must be used in the thermometer and, apart from the greater difficulty in measuring, this involves a number of corrections. We shall endeavour to establish a sound thermodynamic formula for the vapour pressure without making use of the measured p - T relation at the lower end of the scale. To some extent this procedure corresponds to an establishment of the thermodynamic temperature scale in this region, as was done in a similar manner by one of us for solid hydrogen.¹

The Leiden Formulæ.

Soon after Kamerlingh Onnes had succeeded in liquefying helium he determined in 1911 its vapour pressure from 3 mm. to the critical point.² Subsequent extensions of these measurements necessitated investigations of the thermomolecular pressure differences and, in fact, a new determination of the vapour pressure has usually followed each such investigation. Thus, in 1915, Kamerlingh Onnes and Weber³ made a new set of measurements down to 4 mm., which they represented by a formula in which $\log p$ was expressed by a four-term power series in $1/T$. Although this formula contained four constants, its agreement with the observed values was poor.

The discovery of the λ -phenomenon by Keesom and his collaborators showed that it would be inconvenient to represent the vapour pressure by the same formula over the whole range. Thus, after redetermining in 1929 the pressures down to 0.0° , Keesom, Weber, Norgaard and Schmidt⁴ represented their results by two curves of the type:

$$\log p = -A/T + B \log T + C,$$

the constants—three above and three below the λ -point (2.18°)—being empirical and bearing no relation to theory.

In 1932 Keesom⁵ tried to represent these measurements by a thermodynamic formula after having measured in collaboration with Clusius⁶ the specific heats of the liquid. He obtained the following formula as being valid below the λ -point (from now on we deal only with this region):

$$\log_{10} p_{em} = -3.018/T + 2.484 \log_{10} T - 0.000297 T^4 + 1.197. \quad (I)$$

The third term was based on the measurements of the specific heat of the liquid mentioned above, the last term is the theoretical chemical constant, and the first coefficient was chosen so as to give the best

¹ Simon, *Z. Physik*, 1923, **15**, 307.

² Kamerlingh Onnes, *Leiden Comm.*, 1911, No. 119.

³ Kamerlingh Onnes and Weber, *ibid.*, 1915, No. 147b.

⁴ Keesom, Weber and Norgaard, *ibid.*, 1929, No. 202b; Keesom, Weber and Schmidt, *ibid.*, 1929, No. 202c.

⁵ Keesom, *ibid.*, 1932, Supplement No. 71d.

⁶ Keesom and Clusius, *ibid.*, 1932, No. 216b.

agreement with the experimental values.* As can be seen from the construction of the formula, gaseous helium is treated as a perfect gas. We shall see later, however, that the deviations from the ideal state are sufficiently great above about 1.6° to give rise to noticeable corrections.

In 1937 Schmidt and Keesom⁷ published new measurements which were carried out with a very much improved apparatus and the accuracy of these results is probably much superior to that of all preceding data. The authors did not represent their new values by a formula, but gave them in the form of corrections to the 1932 scale. This correction curve is reproduced in Fig. 1, from which it can be seen that the discrepancies between the 1932 and 1937 scales are quite appreciable.

Thermodynamical considerations, however, give rise to some doubt about one part of the correction curve. The latter must comply with

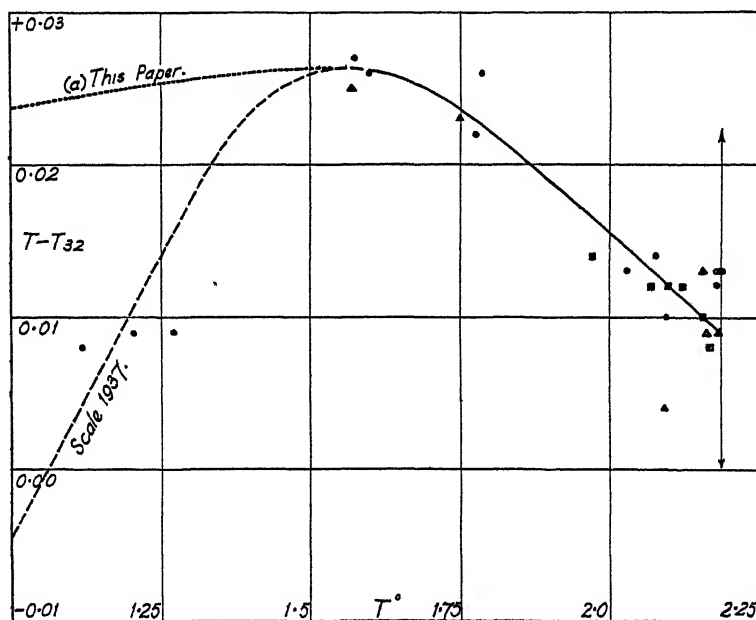


FIG. 1.

the properties of liquid and gas, and therefore the possibilities are limited. In particular, one cannot see how the change in slope below 1.6° can be accounted for, without assuming some quite abnormal behaviour of the gas. There were other reasons which made it doubtful whether the lower part of the correction curve, which was based only on the three points at about 1.2° , was right; in particular, some calibrations of the susceptibility of paramagnetic salts against the vapour pressure suggested that the 1937 scale was some hundredths of a degree too low at 1° K.

* The coefficient of the second term should be $2.5 = C_p/R$, not 2.484 , which corresponds to 1.25 . This error, however, does not affect the results appreciably.

⁷ Schmidt and Keesom, *Physica*, 1937, 4, 963, 971.

Calculation of the Vapour Pressure Curve.

For the thermodynamic calculation we need to know the quantities which determine the entropy of gas and liquid, and at least one point on the p - T curve. If more points on this curve or, alternatively, the latent heat be known, the calculation can be put on a broader basis. We shall discuss the experimental data at our disposal for this purpose.

1. The Entropy of the Gas.

(a) The entropy of an ideal gas is known completely, given either the entropy constant S_0 or the chemical constant i .^{*} There is no reason to suppose that the chemical constant of helium should differ from the theoretical value †

$$i = 3/2 \log_{10} M - 1.588 = -0.685,$$

which corresponds to a singlet ground state in the helium atom. Moreover, a preliminary determination of the chemical constant by Kaischew and Simon⁸ gave a value (-0.62) very near the theoretical value which excluded any deviation of the order $\log 2$. We therefore take the theoretical value for the constant in the vapour pressure formula—as it was also done by Keesom—which equals 1.196 if we now express p in cm. From this value and equation (2) the constants in equation (4) and (5) are calculated.

(b) A more difficult point in the calculation of the entropy of the gas is: how to take into account the imperfections of the gas? This has also to be considered in connection with the temperature coefficient of the heat of evaporation L . This is one of the most important points affecting the accuracy of the scale, as the deviations are extremely large at the higher temperatures (for instance at the boiling-point they amount to 40 %). Before the equation of state is known more accurately it is therefore of little use to calculate L from the vapour pressure by means of the Clausius-Clapeyron equation or dL/dT in the region above the λ -point. But even at 2° the deviations are still large, and our intention, therefore, was to base the calculation on the lowest p - T value possible, so that even if the correction were not known very accurately, it would have little effect on our results.

Experimental data on the equation of state of helium are rather scarce, the measurements at the lowest temperatures being those of Keesom and Kraak,⁹ between 2.5° and 4°. De Boer and Michels¹⁰ have calculated theoretical values in good agreement with the experimental data. On plotting the values of the second virial coefficient B given by de Boer and Michels between 0.9° and 7° against $1/T$ we found that they could be adequately expressed by the formula ‡

$$B = 22 - 380/T \text{ c.c.} \quad . \quad . \quad . \quad . \quad (3)$$

* These two are interconnected by the relation

$$S_0 = C_p + Ri \quad . \quad . \quad . \quad . \quad (2)$$

(if natural logs are used in the corresponding formulæ).

† p in atmospheres, and Brigg's logarithms.

⁸ Kaischew and Simon, *Nature*, 1934, 133, 460.

⁹ Keesom and Kraak, *Physica*, 1935, 2, 37.

¹⁰ De Boer and Michels, *ibid.*, 1939, 6, 409.

‡ We shall use the equation of state in the form

$$pV = RT(1 + B/v).$$

This expression agrees very well with their values, except for the lowest point at 0.9° . Deviations become marked at about 1.3° ; here, however, the corrections which affect our calculations are so small, owing to the low pressure, that they are practically negligible. Hence the influence of the deviations from the perfect gas below this temperature would be noticeable only if the second virial coefficient B began to take up quite extraordinary values, which we see no reason to suspect.

The entropy difference between the real and ideal gas is given by

$$S_{\text{real}} - S_{\text{ideal}} = -p \cdot dB/dT.$$

Hence the total entropy amounts to

$$S = -R \cdot \ln p_{\text{atm.}} + 2.5 R \ln T - p \cdot dB/dT + 1.832 \text{ cal./degree mole} \quad (4)$$

Using Brigg's logarithms and expressing p in cm. Hg this becomes, with the help of equation (3):

$$S = -4.574 \log_{10} p_{\text{cm.}} + 11.435 \log_{10} T - 0.121 p_{\text{cm.}}/T^2 + 10.435 \text{ cal./degree mole} \quad (5)$$

2. The Entropy of the Liquid.

In an earlier calculation of the entropy of the liquid Kaischew and Simon⁸ started from the entropy of the solid, as this could safely be extrapolated to absolute zero, and then using the heats of melting and of expansion a value for the entropy of the liquid was obtained. In the meantime the specific heat of the liquid has been measured down to 0.25° by Pickard and Simon.¹¹ It was found that below 0.8° it follows a T^3 law, within the limits of error, corresponding to a Debye-function of $\theta = 15.5^\circ$. We are therefore in a position to extrapolate to absolute zero, and thus to calculate the absolute value of the entropy; by combining these results with those of Keesom and Miss Keesom¹² (recalculated to the scale 1937) we can now evaluate the entropy up to the λ -point.

3. The Vapour Pressure Curve.

With these data* it is possible in principle to develop an analytical formula, as, for instance, was done in the case of hydrogen. We proceeded, however, in a different way which seemed to demonstrate more explicitly the point at which the 1937 scale becomes invalid:

(1) The latent heat L was calculated from the equation

$$L = T(S_g - S_l),$$

where the 1937 scale was used. The values of L thus obtained are shown as circles in Fig. 2 (Curve 1).

¹¹ Pickard and Simon, *Proc. Roy. Soc. A.* (in the press).

¹² Keesom and Miss Keesom, *Physica*, 1935, 2, 557.

* There exist some preliminary measurements by Dana and Kamerlingh Onnes¹³ of the latent heat of evaporation down to 1.6° . As at this time the phenomenon of the "creeping" film was not yet discovered, we did not feel justified in relying on them at the commencement of our calculation.

¹³ Dana and Kamerlingh Onnes, *Leiden Comm.*, 1926, No. 179c.

(2) The temperature coefficient of the latent heat dL/dT was calculated from the formula

$$\frac{dL}{dT} = C_g - C_l + L \left[\frac{1}{T} - \frac{1}{V_g - V_l} \left(\frac{\partial(V_g - V_l)}{\partial T} \right)_p \right] \quad (6)$$

In this equation we can neglect $\partial V_l/\partial T$ in comparison with $\partial V_g/\partial T$; then, using the equation of state of the gas to eliminate V_g , we obtain

$$\frac{dL}{dT} = C_g - C_l + \frac{L}{T} \cdot \frac{B - T \frac{\partial B}{\partial T} - V_l}{RT/p + B - V_l} \quad (7)$$

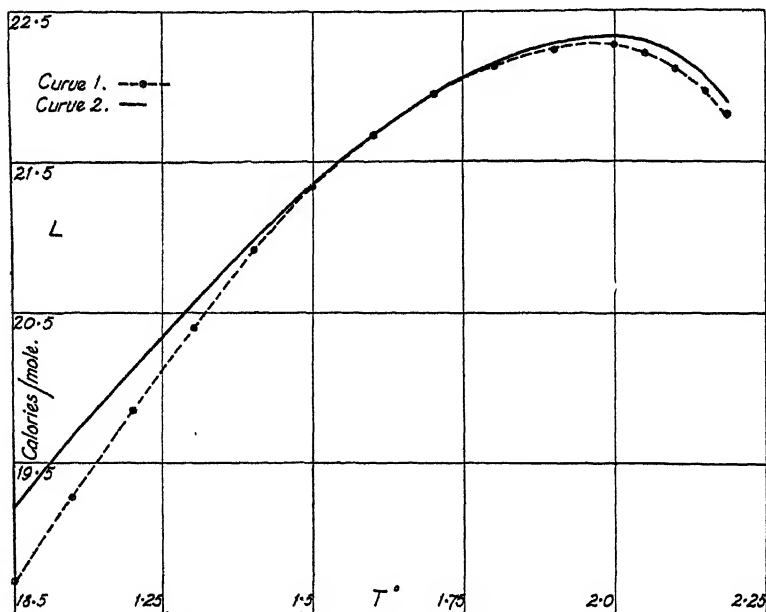


FIG. 2.

The specific heats of the gas and liquid are those measured at constant pressure. For C_g we have

$$C_g = 5R/2 + \int_0^p \left(\frac{\partial C_g}{\partial p} \right)_T dp = 5R/2 - T \int_0^p \frac{\partial^2 B}{\partial T^2} dp,$$

i.e.,
$$C_g = 5R/2 + 0.242 p_{\text{em.}}/T^2 \text{ cal./degree mole.}$$

The measurements of the specific heat of the liquid by Pickard and Simon, and Keesom and Miss Keesom give, of course, the specific heat at the saturation vapour pressure. Calculation from data of Keesom of the error introduced by using this instead of C_p shows that, even at the λ -point, where it is greatest, the error is about 1 per cent.

Integrating equation (7) we obtain an L - T curve (shown in Fig. 2 as a continuous line (curve 2)) which is known except for an additive constant.* If the 1937 scale is thermodynamically consistent, it should be possible to shift curve 2 to coincide with curve 1. We see from Fig. 2 that this is not possible. As in the region above 1.6° the deviations

* The absolute values of L , and also of p , affect the last term in equation (7) but, below 1.6° , this term is small in comparison with the others.

from the ideal state may still have a marked influence and, the correction being somewhat uncertain, we thought it safer to adjust both curves to the same value at 1.6° . Moreover, the magnetic experiments had shown that at 1.6° the 1937 scale was substantially correct (see also measurements by Casimir, de Haas and de Klerk).¹⁴ It is evident from Fig. 2 that at the lower temperatures appreciable differences in the two curves for L (0.5 cal. at 1°) appear. From curve 1 (*i.e.* from the entropies) dL/dT has a value of 5.6 cal./deg. mole, while it follows from the specific heats that it must be about one calorie/degree smaller.

The next step was to take curve 2 as a basis for the calculation of the vapour pressures below 1.6° by putting

$$S_g = S_l + L/T,$$

where L is now derived from curve 2. Above 1.6° , however, we retained the 1937 scale, as it was not impossible that the differences between the two curves would disappear if the specific heat of the liquid were changed

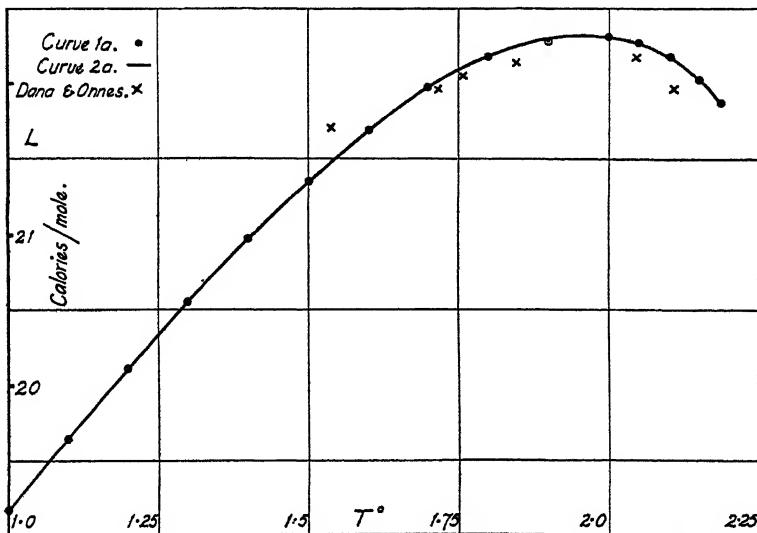


FIG. 3.

at the lower temperatures according to the new scale. The latter, which we intended to be a first approximation, was used to recalculate the values of C_l , and hence S_l (above 1.6° the alteration in S_l amounted to -0.032 cal./deg.). Also, of course, some of the correction terms in which L and p occur were slightly changed. These alterations affected both L and dL/dT and the recalculated curves (1a) and (2a) are shown in Fig. 3; we see that they coincide almost exactly, the previous discrepancy at the higher temperatures having disappeared owing to the change in the entropy of the liquid. We have thus arrived at an accurate p - T relation and a second recalculation is unnecessary.*

¹⁴ Casimir, de Haas and de Klerk, *Physica*, 1939, 6, 241.

* We find that if we calculate L and dL/dT neglecting the second virial coefficient, the maximum discrepancy which appears between curves (1a) and (2a) in the region between 1° and 1.6° is only 0.04 calories, corresponding to 2% in the vapour pressure. It is obvious, therefore, that even relatively large errors in our assumed B - T relation could not seriously affect the calculated vapour pressure in this region.

Comparing these values of L with the direct experimental values of Dana and Kamerlingh Onnes (after adjusting their temperatures to the 1937 scale), shown as crosses in Fig. 3, we observe that the greatest deviation is only $\frac{1}{2}\%$, which is certainly within the experimental error of these determinations.

We can now write the formula for the vapour pressure in the following way :

$$\log_{10} p = -L_0/4.574T + C_p/R \cdot \log_{10} T - f(T) + i + \Delta \quad (8)$$

L_0 is found from the values above to be 14.2_6 cal./mole. The second and fourth terms need no discussion; the third term is $\frac{1}{4.574} \int_0^T \frac{C_1 dT}{T^2}$.

For the sake of simplicity we shall not insert the experimental values of C_1 over the whole range, as they cannot be expressed in an explicit form.

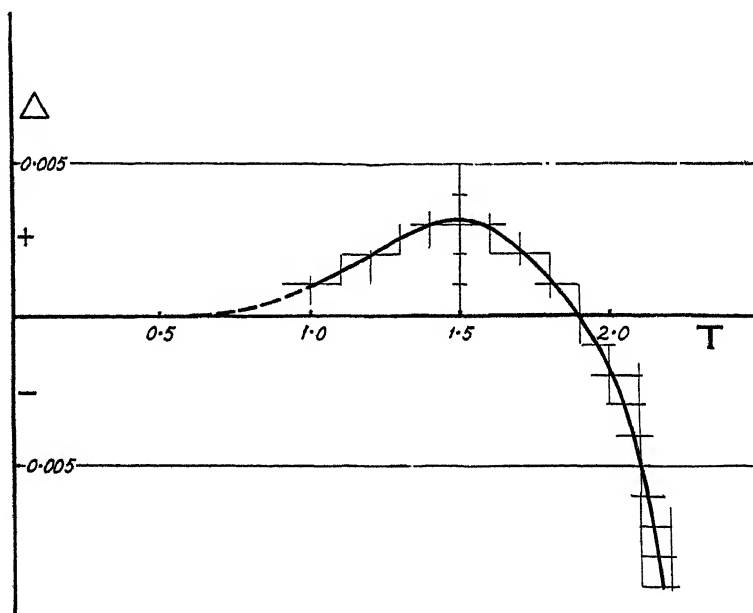


FIG. 4.

We replace them by the limiting T^3 part of the specific heat, corresponding to a Debye θ of 15.5° . The differences between this term and that which would correspond to the actual specific heats are combined with the contributions from the imperfection of the gas to form the term Δ , shown in Fig. 4.

Equation (8) therefore becomes

$$\log_{10} p_{\text{em.}} = -3.117/T + 2.5 \log_{10} T - 0.00227 T^3 + 1.196 + \Delta \quad (9)$$

The maximum amount by which the correction Δ affects the vapour pressure is 5% at the λ -point. Below 1.4° the combined effect of the T^3 term and Δ is less than 1% on the vapour pressure, so that we can then write :

$$\log_{10} p_{\text{em.}} = -3.117/T + 2.5 \log_{10} T + 1.196 \quad (T = 0 - 1.4^\circ) \quad (10)$$

In the following table a number of vapour pressures are calculated from our results and from the 1932 and 1937 scales.

Above 1.6° the 1937 scale and our scale are identical. We do not want, however, to emphasise this agreement too much, as an experimental determination of B in this region may alter the situation, although the differences to be expected cannot be very big.

Below 1.6°, however, the deviations from the ideal state cannot influence the p - T relation to any appreciable extent and we believe that our scale, which differs noticeably from the 1937 scale at its lower end (see also Fig. 1) deserves preference over the latter.

TABLE I.

T .	$p_{\text{cm. (1932)}}$	$p_{\text{cm. (1937)}}$	$p_{\text{cm. (this paper)}}$
2.186	3.91	3.83	
2.1	3.18	3.10	
2.0	2.45	2.33	
1.9	1.83	1.72	
1.8	1.33	1.23	
1.7	0.93	0.85	
1.6	0.643	0.565	0.565
1.5	0.405	0.359	0.358
1.4	0.244	0.218	0.215
1.3	0.141	0.128	0.120
1.2	0.0747	0.0695	0.0624
1.1	0.0356	0.0348	0.0292
1.0	0.0150	0.0155	0.0120

In this region the 1937 scale depends only on a group of three points near 1.2° (which correspond to a pressure about 10 % higher than ours), so that an experimental error in these points would remove the whole difference. One may surmise that the "creeping" film may be responsible for it, as discussed by Rollin and Simon,¹⁵ and by Daunt and Mendelssohn.¹⁶

This film will evaporate at some higher point of the tube and thus create a pressure difference between the upper and lower part of it. One can calculate the order of magnitude of the increase of pressure (Δp) to be expected and arrive at the following formula: *

$$\frac{\Delta p}{p} \approx 2 \cdot 10^{-10} \frac{l_{\text{cm.}}}{r^2 \text{cm.}} \frac{T^2}{p^2} (\text{cm.}),$$

where l is the length in cm. of the tube between the place of evaporation of the film and the surface of the liquid and r its radius. Taking the dimensions as shown in Schmidt and Keesom's paper, this formula gives an increase of pressure of only 0.2 %, so that this explanation would not hold unless perhaps the tube contained a constriction not visible in the diagram.

TABLE II.

T .	$p_{\text{cm.}}$	$L_{\text{cal./mol.}}$
1.0	1.20×10^{-2}	19.1 ₈
0.95	7.20×10^{-3}	18.9 ₄
0.9	4.13×10^{-3}	18.7 ₀
0.85	2.24×10^{-3}	18.4 ₆
0.8	1.14×10^{-3}	18.2 ₁
0.75	5.35×10^{-4}	17.9 ₇
0.7	2.26×10^{-4}	17.7 ₂
0.6	2.79×10^{-5}	17.2 ₂
0.5	1.6×10^{-6}	16.7 ₃
0.4	2.6×10^{-8}	16.2 ₃
0.3	3.2×10^{-11}	15.7 ₄
0.2	7.4×10^{-16}	15.2 ₄
0.1	3.4×10^{-23}	14.7 ₅
0.05	4×10^{-65}	14.5 ₁
0.01	3×10^{-314}	14.3 ₁
0	0	14.2 ₆

It is, of course, desirable to subject the calculated formula to an experimental test. One of us (B. B.) with R. A. Hull has commenced

¹⁵ Rollin and Simon, *Physica*, 1939, 6, 219.

¹⁶ Daunt and Mendelssohn, *Proc. Roy. Soc., A*, 1939, 170, 439.

* We extrapolated the measurements of the viscosity of the gas of van Itterbeek and Keesom¹⁷ as being proportional to T .

¹⁷ van Itterbeek and Keesom, *Physica*, 1938, 5, 257.

such experiments, using the susceptibility of a paramagnetic salt as thermometer, and we may mention that the preliminary results show good agreement with the calculated values. In any case, should small alterations be called for, we have given the essential data whereby the corresponding interpretation in terms of the vapour pressure curve can quickly be obtained.

In Table II. we give a few data of the vapour pressure and latent heat of evaporation calculated from equation (9) and (7) which may be useful.

It may be mentioned that the lowest pressure reached by Keesom¹⁸ by pumping off liquid helium (0.0036 mm. Hg) corresponds on this scale to a temperature of 0.72_8° compared with 0.70_7° on the 1932 scale.

The Chemical Constant.

The very good consistency we now obtain for the whole curve below the λ -point, and also the good agreement with the experimental values of L , show that our assumptions concerning the difference of entropy of the two phases were justified. This is equivalent in this particular case to the statement that the value of the chemical constant which we assumed is correct and from our calculations we see that the probable error is not greater than 0.01.

Summary.

A rational vapour pressure curve for helium below the λ -point is calculated; from the λ -point down to 1.6° it is in good agreement with the values of Schmidt and Keesom, but then deviates towards lower pressures. Tables and diagrams of the vapour pressure and latent heat are given.

It follows from these calculations that the chemical constant of helium is within 0.01 of the theoretical value.

*Clarendon Laboratory,
Oxford.*

¹⁸ Keesom, *Leiden Comm.*, 1932, No. 219a.

REVIEWS OF BOOKS.

Rheology of Suspension. By H. L. RÖDER. A Thesis for the University of Utrecht published in English by H. J. Paris. Amsterdam, 1939. Pp. xiv + 86.

This little booklet describes in detail the author's own measurement in this field of colloid chemistry, a field which has again come into prominence. While his method of measurement of dilatancy marks a distinct advance, it and that used for thixotropic systems may be criticised for being dependent on the instrument used. The results have, however, yielded valuable information as to the conditions which govern whether a system will be thixotropic or dilatant.

C. F. G.

Electron Optics in Television. By I. G. MALOFF and D. W. EPSTEIN.
(McGraw-Hill Publishing Company Ltd. Pp. xi + 299. 21s. net.)

Electron Optics. By OTTO KLEMPERER. (Cambridge University Press. Pp. x + 107. 6s. net.)

The first of these books is by two well-known workers in the subject, both members of the Research Division of the R.C.A. It is concerned with the theory of electron optics and its application to the television cathode ray tube, and, as the authors state in their preface, should not be considered an exhaustive treatment of the subject, but rather an account of that part of it with which the authors have had first-hand experience at the Research Laboratories of the R.C.A. The treatment is divided into an Introduction, a Part I on electron optics, and a Part II on the television cathode ray tube. The introduction contains a description of the cathode ray television system and refers to a few other applications of electron optics. The first chapter of Part I deals with fundamental concepts such as the electron, the main result of the kinetic theory of gases and the various degrees of vacua in terms of the mean free path, number of collisions, etc. The second chapter refers to the main facts of electron emission. Although the introduction and these two chapters contain an interesting summary of the facts and some useful tables, one is bound to say that these can be obtained for the most part from elsewhere and that for the persons who are likely to read this book the introductory matter useful for the understanding of the remainder could have been summarised in considerably less than 66 pages. The theory of electron optics is then commenced in Chapter III with the analogy between electron optics and light. The treatment which follows is throughout concerned with the case of axial symmetry. The potential distribution is worked out in terms of the potential function along the axis and its even derivatives. The equations of motion of the electron and the differential equation of its trajectory are then developed. This is followed by an explanation of the calculation of paraxial trajectories using the experimental data of the axial distribution of potential from which the first and second derivatives (and for one form of the method the radius of curvature of the equipotential surfaces where they cross the axis) are obtained. Solutions of the trajectory equation or of the equations of motion are then found for successive potential layers and hence the ray is traced. The cardinal points are then considered, the focal lengths and magnification of a thin lens being worked out in terms of the axial potential function and its derivatives. It would have been worth while here to have made some reference to the way in which the potential field is plotted.

Chapter VI is on electrostatic lenses and in particular on how the cardinal points are affected by the size and length of the anodes and by the voltage ratio. This discussion is illustrated by a number of excellent graphs and altogether this is a useful and interesting chapter, though beam crossover might have been dealt with more clearly and fully. Chapter VII is about defects of electron focussing, only spherical aberration and the effect of space charge being discussed in any detail. Chapter VIII, the last of Part I, develops the theory of magnetostatic focussing briefly on the same lines as those adopted for electrostatic focussing.

Part II opens with three chapters on the electron gun, the deflection of electron beams and luminescent screens respectively. That on the electron gun, again, has a number of excellent graphs showing the effect of a number of the gun variables such as grid spacing, aperture and skirt length, and first anode voltage on the dependent variables such as cut-off voltage, total and beam current and width of scanning line. The remainder of the book is taken up mainly with a chapter on "Accessories." The characteristics of a dynatron oscillator and a blocking oscillator are referred to and a description is given of the isocline method of calculating the characteristics of a multi-vibrator and a blocking oscillator. There is then a brief reference to synchronisation of impulse generators and to the inverse method of calculating vacuum tube performance. Although the account to the isocline method is interesting enough, this part of the book is too sketchy to be of much value.

The second book, compiled and written by Otto Klemperer, is based in part on reports of research work performed in the E.M.I. Research Laboratories. Naturally, in a book of its size, the treatment is not so detailed as with the first book, but there is at the end an excellent summary of the literature of the subject and the book is well written. The major part covers much the same ground as Part I of the first book, though the treatment is different. The equation of the electron trajectory is not developed and the calculation of the ray path follows different lines. As before, the field is divided up into a number of potential layers, but the path is found trigonometrically from direct measurements of the radii of curvature of the potential surfaces. An account is given of the method of Picht and a mention is made of that of Maloff and Epstein referred to above. The treatment of magnetic lenses is again different, use being made of the meridional potential. And, whereas in the first book the Busch formula for the focal length of a thin magnetostatic lens is deduced from the differential equation of the trajectory of paraxial electrons, in the second book the simplified method of Bouwers is used. Although the latter has a brief chapter on practical applications of electron optics, it contains nothing to correspond with Part II of the former, but in the region where the two books overlap, they are complementary and may usefully be read together.

K. J.

CORRIGENDA.

- Page 906, line 12. *For carbon-hydrogen read carbon-carbon.*
 ,, 911, ,, 15. *For cis-trans-compound read cis-compound.*
 ,, 919, ,, 6. *For C₁₆H₂ read C₆H₁₂.*
 ,, 979. *For title of Section C read "Ring Closure and Isomerisation".*
 ,, 1053, line 27. *For "one example only on" read "one example only: of".*

THE ACTIVITY COEFFICIENTS OF SOME ALKALI HALIDES AT 25°

By R. A. ROBINSON.

Received on 12th April, 1939.

The isopiestic vapour pressure method has been applied^{1, 2, 3} to the determination of the activity coefficients of forty-one salts in aqueous solution at 25°. As a reference salt potassium chloride was chosen and a set of activity coefficients selected somewhat arbitrarily from the data then available for this salt. In a succeeding communication * I shall describe the use of the isopiestic method at temperatures between 15° and 60° and apply the results to the calculation of the heat content and heat capacity of sodium and potassium chloride solutions. Before this can be done, however, it will be necessary to review the data for potassium chloride at 25° with the object of removing the arbitrariness of the set of activity coefficients originally selected for this salt.

Potassium Chloride—Sodium Chloride at 25°.

In the course of trying various minor modifications of the isopiestic vapour pressure method 75 determinations were made of the isopiestic ratio between these two salts employing (a) silver dishes, (b) gold-plated dishes, (c) stainless steel dishes and (d) platinum crucibles sunk in holes in the copper block. No difference could be detected under these varying conditions. The results are too numerous to be reproduced here in detail but may be expressed accurately by a curve of the isopiestic ratio ($m_{\text{KCl}}/m_{\text{NaCl}}$ of equal vapour pressure) against m_{NaCl} , drawn through the following points:

m_{NaCl}	0.1	0.2	0.3	0.5	0.7
$m_{\text{NaCl}}/m_{\text{KCl}}$	1.006	1.011	1.016	1.024	1.031

Between 1 M. and 4 M. — NaCl the equation:

$$m_{\text{KCl}}/m_{\text{NaCl}} = 1.0082 + 0.03237 m_{\text{NaCl}}$$

is valid.

The results are on the average 0.0015 lower in the isopiestic ratio than those obtained by Robinson and Sinclair.¹ The average deviation from the results of Scatchard, Hamer and Wood⁴ is 0.0006 between 0.5 and 4 M. NaCl, but their results are approximately 0.002 higher at lower concentrations. In previous investigations I have used potassium chloride as standard; there is one disadvantage with this salt in that

¹ Robinson and Sinclair, *J. Amer. Chem. Soc.*, 1934, **56**, 1830.

² Robinson, *ibid.*, 1935, **57**, 1161, 1165; 1937, **59**, 84; Robinson and Jones, *ibid.*, 1936, **58**, 950.

³ Robinson, *Trans. Faraday Soc.*, 1938, **34**, 1142.

* This vol., page 1220.

⁴ *J. Amer. Chem. Soc.*, 1938, **60**, 3061.

solutions which are isopiestic with potassium chloride solutions 4.0 to 4.8 m. in concentration (*e.g.*, sodium chloride between 3.5 and 4.0 m.) can only be made to yield an activity coefficient by an extrapolation of the activity coefficient curve of potassium chloride beyond 4 m. As Harned and Cook⁵ have recently recalculated the data of Harned and Nims⁶ for sodium chloride, I decided to combine their activity coefficients for sodium chloride with the above isopiestic data in order to obtain the activity coefficient of potassium chloride which can then be compared with similar values given by Harned and Cook⁷ and by Shedlovsky and MacInnes.⁸

TABLE I.—ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM CHLORIDE AT 25°.

m.	Sodium Chloride.	Potassium Chloride.			$\gamma_{\text{NaCl}}/\gamma_{\text{KCl}}$	
		R.	H.	S.	R.	H.
0.1	0.779	0.770	0.769	0.7701	1.011	1.013
0.2	.733	.718	.719	.7191	1.022	1.020
0.3	.708	.687	.688	.6875	1.031	1.032
0.5	.681	.650	.651	.6516	1.048	1.046
0.7	.667	.627	.628	.629	1.064	1.068
1.0	.658	.607	.606	.6069	1.084	1.084
1.5	.657	.585	.585	.587	1.123	1.122
2.0	.671	.577	.576	.5781	1.163	1.165
2.5	.692	.574	.572	.574	1.206	1.210
3.0	.720	.575	.571	.5741	1.253	1.261
3.5	.753	.578	.574	.5765	1.302	1.312
4.0	.793	.583	.579	.5806	1.360	1.368
4.5	—	.591	—	—	—	—

The second column of Table I contains the activity coefficients of sodium chloride given by Harned and Cook⁵ for sodium chloride; the data in the next three columns refer to the activity coefficient of potassium chloride calculated from the former by means of the isopiestic data, from the e.m.f. data of Harned and Cook⁷ and from the results of Shedlovsky and MacInnes⁸ respectively. The degree of concordance is shown in the last two columns which give the ratio of the activity coefficients of the two salts according to isopiestic data and to Harned's e.m.f. data respectively. The agreement is excellent below 3 m., above this there is a divergence corresponding to approximately 0.004 in the activity coefficient.

Potassium Chloride—Sodium Bromide at 25°.

Experiments were made with both gold-plated silver dishes and platinum crucibles. The same result was obtained in each case, a result which, moreover, agreed with the previous determination. Table II gives the molalities of isopiestic solutions of these two salts, the first of each pair of figures referring to potassium chloride.

⁵ *J. Amer. Chem. Soc.*, 1939, 61, 495.

⁷ *Ibid.*, 1937, 59, 1290.

⁶ *Ibid.*, 1932, 54, 423.

⁸ *Ibid.*, 1937, 59, 503.

TABLE II.

0.3751,	0.3640;	0.4743,	0.4589;	0.6442,	0.6156;	0.6434,	0.6164;
0.6609,	0.6322;	0.6660,	0.6358;	0.6955,	0.6655;	0.7705,	0.7328;
0.8378,	0.7950;	0.8724,	0.8250;	0.9408,	0.8856;	1.1337,	1.238;
1.347,	1.243;	1.363,	1.258;	1.389,	1.282;	1.768,	1.609;
2.324,	2.069;	2.552,	2.257;	2.841,	2.483;	3.193,	2.764;
3.232,	2.794;	3.366,	2.894;	3.366,	2.898;	3.557,	3.044;
3.812,	3.239;	3.831,	3.258;	3.842,	3.265;	3.937,	3.337;
4.048,	3.422;	4.084,	3.446;	4.167,	3.508;	4.243,	3.566;
4.573,	3.804;	4.599,	3.827;	4.782,	3.956;	4.811,	3.984.

Potassium Chloride—Potassium Bromide at 25°.

These measurements were made entirely with the platinum crucibles, the isopiestic ratio, ($m_{\text{KBr}}/m_{\text{KCl}}$) being found to be slightly higher than that reported previously; this is attributed to some corrosion of the silver dishes in the earlier experiments, although it is evident from the magnitude of the difference between the two results that this corrosion must have been small compared with that obtained with the heavier alkali salts. The results are given in Table III.

TABLE III.

0.2108,	0.2104;	0.3751,	0.3730;	0.5570,	0.5535;	0.5913,	0.5873;
0.8442,	0.8362;	1.071,	1.059;	1.486,	1.467;	1.517,	1.496;
1.863,	1.835;	2.110,	2.075;	2.768,	2.722;	2.887,	2.841;
3.144,	3.090;	3.158,	3.105;	3.185,	3.131;	3.335,	3.274;
3.396,	3.337;	3.942,	3.872.			3.346,	3.295;

Using the activity coefficients of potassium chloride obtained above I have evaluated the activity coefficients of these two bromides in Table IV.

TABLE IV.—ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM BROMIDE AT 25°.

m .	γ_{NaBr}	$\gamma_{\text{NaBr}}/\gamma_{\text{KCl}}$		γ_{KBr}	$\gamma_{\text{KBr}}/\gamma_{\text{KCl}}$	
0.1	0.782	1.018	1.017	0.772	1.003	1.004
0.2	.740	1.031	1.029	.722	1.006	1.004
0.3	.718	1.045	1.044	.692	1.008	—
0.5	.697	1.071	1.068	.658	1.013	1.013
0.7	.689	1.098	1.094	.637	1.017	—
1.0	.690	1.136	1.132	.620	1.021	1.019
1.5	.704	1.204	1.202	.602	1.029	1.026
2.0	.735	1.273	1.274	.598	1.036	1.032
2.5	.773	1.347	1.352	.598	1.042	1.039
3.0	.820	1.427	1.447	.602	1.047	1.043
3.5	.873	1.511	1.530	.607	1.051	1.053
4.0	.939	1.610	1.613	.615	1.056	1.061

The ratio columns give the ratio of the activity coefficients of the bromide to potassium chloride using first the isopiestic data and secondly the e.m.f. data of Harned and Cook ⁷ for potassium chloride, Harned

and Crawford⁹ for sodium bromide and Harned¹⁰ for potassium bromide. The agreement is very satisfactory up to a concentration of 3 M.

Summary.

These considerations may be summarised as follows: a set of activity coefficients of potassium chloride is assumed which agree with the e.m.f. determinations of Harned and Cook and of Shedlovsky and MacInnes. The deviation from the former is not more than 0.001 in γ up to 2.5 M. and is 0.004 between 3 M. and 4 M. Up to 2.5 M. the agreement with the data of Shedlovsky and MacInnes is nearly as good and better agreement obtains between 3 M. and 4 M. Isopiestic data then give a set of activity coefficients for sodium chloride identical with that of Harned and Cook, provided that a suitable extrapolation is made for γ_{KCl} at 4.5 M. The isopiestic data also give excellent agreement with the data of Harned and Crawford on sodium bromide, except at 3 M. and 3.5 M., where their results are 0.005 higher in γ than mine. Good agreement between the isopiestic data and the e.m.f. results of Harned for potassium bromide is obtained over the whole concentration range. The activity coefficients given for these four salts are therefore consistent among themselves as regards both isopiestic and e.m.f. experiments.

The ratio $\gamma_{NaCl}/\gamma_{KCl}$ given by the data of Scatchard, Hamer and Wood⁴ is approximately 0.005 higher than mine; this is due largely to the fact that my curve of m_{NaCl}/m_{KCl} against m_{NaCl} is drawn somewhat lower than theirs at low concentration and that they rely on γ_{NaCl} at 0.2 M. from freezing-point results whereas I have been influenced by the e.m.f. value of γ_{NaCl} at 0.1 M. given by Brown and MacInnes.¹¹

Finally it may be noted that the values I have now selected for γ_{KCl} are uniformly higher than those given by Robinson and Sinclair;¹ thus activity coefficients previously reported may be converted to the new standard by multiplying by the ratio 0.770/0.766. This would not apply in the case of cobalt chloride, which requires no correction since the data of Shedlovsky and MacInnes for potassium chloride were used.

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⁹ *J. Amer. Chem. Soc.*, 1937, 59, 1903.

¹⁰ *Ibid.*, 1929, 51, 416.

¹¹ *Ibid.*, 1935, 57, 1356.

THE RELATIVE OSMOTIC COEFFICIENTS OF SODIUM AND POTASSIUM CHLORIDE IN DEUTERIUM OXIDE AT 25°.

By R. A. ROBINSON.

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The substitution of deuterium oxide for ordinary water in a protolytic equilibrium results in a marked effect. Thus La Mer and Chittum¹ found that the dissociation constant of acetic acid in deuterium oxide was about a third of that found in ordinary water as solvent, and Wynne-Jones² found the dissociation constant of the solvent itself to be about five times less. It would be expected that in cases where the solvent does not enter into a protolytic equilibrium the effect of such a

¹ *J. Amer. Chem. Soc.*, 1936, 58, 1642.

² *Trans. Faraday Soc.*, 1936, 32, 1397.

change of solvent would be much less, *e.g.*, there should be little effect on the osmotic or activity coefficients of a salt in passing from one solvent to the other.

The isopiestic ratio of potassium chloride to sodium chloride (the ratio $m_{\text{KCl}}/m_{\text{NaCl}}$ of solutions of the same vapour pressure) has been well established by Robinson and Sinclair³ and by Scatchard, Hamer and Wood,⁴ and has been confirmed by some further measurements from this laboratory,⁵ so that there can be little doubt as to the values of this isopiestic ratio at 25° between 0.1 and 4 m. NaCl. These are, therefore, a suitable pair of salts to study in deuterium oxide solution, and this paper describes some measurements of an exploratory nature of these salts in heavy water.

The deuterium oxide contained 99.6 % D₂O; the salts were highly purified and were used in a comparative series of measurements with ordinary water as solvent. The following solutions (Table I) were found to be isopiestic, the first of each pair of figures being the molality of potassium chloride (mols. KCl per 1000 g. D₂O) and the second that of sodium chloride.

TABLE I.

0.5238,	0.5111;	0.5306,	0.5172;	1.076,	1.026;	1.270,	1.200;	1.316,	1.245;
1.804,	1.680;	2.235,	2.054;	2.280,	2.097;	2.348,	2.154;	2.506,	2.292;
2.513,	2.291;	2.761,	2.500;	3.053,	2.741;	3.200,	2.862;	3.242,	2.902;
3.395,	3.024;	3.613,	3.195;	3.703,	3.279;	3.932,	3.453.		

A plot of the isopiestic ratios against the *molality* of sodium chloride shows that the ratio is considerably higher in deuterium oxide than in water at the same molality, the difference increasing with increasing salt concentration. Thus at 3 m. NaCl the isopiestic ratio is 1.105 in H₂O and 1.122 in D₂O. This difference is, however, to a certain extent illusory, because the use of the concentration unit of a mol. in a 1000 g. of solvent makes no allowance for the 10 % difference in a molecular weight of the solvent. A fairer comparison can be made if the concentrations are expressed in mol. ratios of salt to solvent (Table II). There remains therefore a much smaller difference between

TABLE II.

Mol. Ratio of NaCl	Molality in		Isopiestic Ratio in	
	H ₂ O.	D ₂ O.	H ₂ O.	D ₂ O.
0.01	0.5551	0.4993	1.0255	1.026
0.02	1.110	0.9986	1.044	1.047
0.03	1.665	1.498	1.062	1.066
0.04	2.220	1.997	1.080	1.084
0.05	2.775	2.497	1.098	1.103
0.06	3.331	2.996	1.116	1.121

the isopiestic ratios at corresponding mol. ratios, which implies that the ratios of the osmotic coefficients, $\phi_{\text{NaCl}}/\phi_{\text{KCl}}$ are almost but not quite

³ *J. Amer. Chem. Soc.*, 1934, **56**, 1830.

⁴ *Ibid.*, 1938, **60**, 3061.

⁵ Robinson, *Trans. Faraday Soc.*, 1939, **35**, 1217.

the same at corresponding mol. ratios, there being a difference in these osmotic ratios of 0.5 % at the highest concentrations. Thus if there is an increase in the osmotic coefficient of potassium chloride on substituting heavy water for light water, there must be a 0.5 % greater increase in the osmotic coefficient of sodium chloride. There being only 0.37 % difference in the dielectric constants of these two solvents,⁶ it would be anticipated that the change of solvent would have little effect on the osmotic coefficient of either salt, in which case the ratios of the osmotic coefficients would not be markedly different. This is what is found. The converse is not strictly true, but it might be held that if the osmotic coefficients of both salts are considerably different in the two solvents, then it is unlikely that these changes will be so parallel that the ratio of the two osmotic coefficients will only alter by 0.5 %. Further discussion would not be profitable, as any prediction of the effect of a change of dielectric constant on the osmotic coefficient involves a knowledge of volume concentrations and the necessary density data for D₂O solutions are not available. This preliminary investigation does, however, suggest that a determination by an e.m.f. method of the activity coefficient of a suitable salt such as cadmium sulphate in deuterium oxide would afford a standard from which the activity coefficients of a number of univalent salts could be obtained by the isopiestic method, and these data, supplemented by density measurements, would afford interesting information about the linear term in the extended Debye-Hückel equation.

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⁶ Wyman and Ingalls, *J. Amer. Chem. Soc.*, 1938, 60, 1182.

THE HEAT CONTENT AND HEAT CAPACITY OF SODIUM CHLORIDE SOLUTIONS.

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Received 23rd May, 1939.

The isopiestic ratio of sodium and potassium chloride has been measured at 5° intervals between 15° and 60°, a metal desiccator being used for temperatures above 40°. About thirty measurements were made at each temperature except 25°. The results above 1 m. NaCl may be expressed as the following isopiestic ratio:

$$m_{\text{KCl}}/m_{\text{NaCl}} = 1.00633 + 0.00019(t - 15) + [0.03337 - 0.0001(t - 15)] m_{\text{NaCl}}.$$

Below 1 m. NaCl the small effect of temperature on the isopiestic ratio may be expressed by combining the data in a previous paper¹ valid at 25° with a temperature coefficient of 0.0001 m_{NaCl} per degree.

As in the use of the isopiestic method to determine the activity coefficient of a salt it is necessary to have information about the activity coefficient of a reference salt, so in the application of this method to measurements of heat contents and heat capacities it is necessary to

¹ Robinson, *Trans. Faraday Soc.*, 1939, 35, 1217.

know the heat content and heat capacity of a reference salt. Thus if the necessary thermal data for potassium chloride were available it would be possible to use isopiestic data to obtain the activity coefficients of sodium chloride between 15° and 60° and thence to calculate the partial molal heat content and heat capacity of sodium chloride. Unfortunately, for neither of these salts is the thermal data complete over the entire concentration range, although the recent application of the boiling-point method by Smith² to determine the activity coefficient of sodium chloride between 0.1 and 1 M. NaCl from 60° to 100°, the e.m.f. measurements of Harned and Nims³ as recalculated by Harned and Cook,⁴ covering the temperature range 0° to 40° and the thermal measurements of Rossini,⁵ A. L. Robinson,⁶ Gulbranson and A. L. Robinson,⁷ and Young and Vogel⁸ form a considerable contribution to the thermodynamics of sodium chloride solutions. In addition, there are available the results of Harned and Cook⁹ and of Rossini⁵ on potassium chloride solutions.

Between 0.1 and 1.0 M. KCl the partial molal heat contents and heat capacities given by Harned and Cook and by Rossini are in reasonable agreement, and it makes little difference which set of data are combined with values of γ_{KCl} at 25° given in a preceding paper¹ in order to calculate values of γ_{KCl} between 15° and 60°. Moreover both sets of data lead to values of γ_{KCl} at 100° which are in fair agreement with γ_{KCl} obtained at this temperature by Saxton and Smith¹⁰ from boiling-point measurements. For concentrations up to 1 M. KCl therefore, the calculation can be carried out with confidence, but above this concentrations the thermal data of Rossini diverge from those of Harned and Cook, the former being in better agreement with the results of Saxton and Smith at 100°. Thus it may not be correct to extrapolate γ_{KCl} between 45° and 60° from the data of Harned and Cook, their results being obtained from the "least squares" method on data between 0° and 40°. Unfortunately Rossini's data go only to 2 M. KCl. I have therefore calculated γ_{KCl} between 15° and 60° from the heat contents and heat capacities given by Harned and Cook and combined these with the isopiestic data to obtain the activity coefficient of sodium chloride between 15° and 60°. The activity coefficients between 0.1 and 1 M. are given in Table I and plotted in Fig. 1. I have also used the

TABLE I.—THE ACTIVITY COEFFICIENT OF SODIUM CHLORIDE AS ($1 + \log \gamma$) BETWEEN 15° AND 60° FROM 0.1 TO 1 M.

m.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
0.1	0.8922	0.8919	0.8914	0.8908	0.8902	0.8893	0.8885	0.8874	0.8861	0.8848
0.2	.8656	.8653	.8652	.8647	.8641	.8634	.8624	.8614	.8599	.8586
0.3	.8495	.8501	.8502	.8499	.8496	.8490	.8480	.8470	.8456	.8438
0.5	.8318	.8328	.8334	.8332	.8333	.8328	.8319	.8310	.8295	.8277
0.7	.8210	.8230	.8239	.9245	.8249	.8248	.8243	.8236	.8220	.8204
1.0	.8141	.8165	.8185	.8194	.8203	.8206	.8203	.8197	.8183	.8163

² *J. Amer. Chem. Soc.*, 1939, 61, 500.

³ *Ibid.*, 1932, 54, 423.

⁴ *Ibid.*, 1939, 61, 495.

⁵ *Bur. Stand. J. Res.*, 1931, 6, 791; 1931, 7, 47.

⁶ *J. Amer. Chem. Soc.*, 1932, 54, 1311.

⁷ *Ibid.*, 1934, 56, 2637.

⁸ *Ibid.*, 1937, 59, 1290.

⁹ *Ibid.*, 1932, 54, 3030.

¹⁰ *Ibid.*, 1932, 54, 2626.

data of Rossini at 1.5 and 2 M. and the results are plotted in Fig. 2 along with those obtained with the aid of the thermal data of Harned and Cook for potassium chloride. I have felt justified in quoting results at 1 M. and less to four decimal places because, although such absolute accuracy is not claimed, the relative temperature variation is correct to this extent.

The accuracy of these figures may be tested in three ways. A comparison can be made of the ratio $\gamma_{\text{NaCl}}/\gamma_{\text{KCl}}$ at similar concentrations

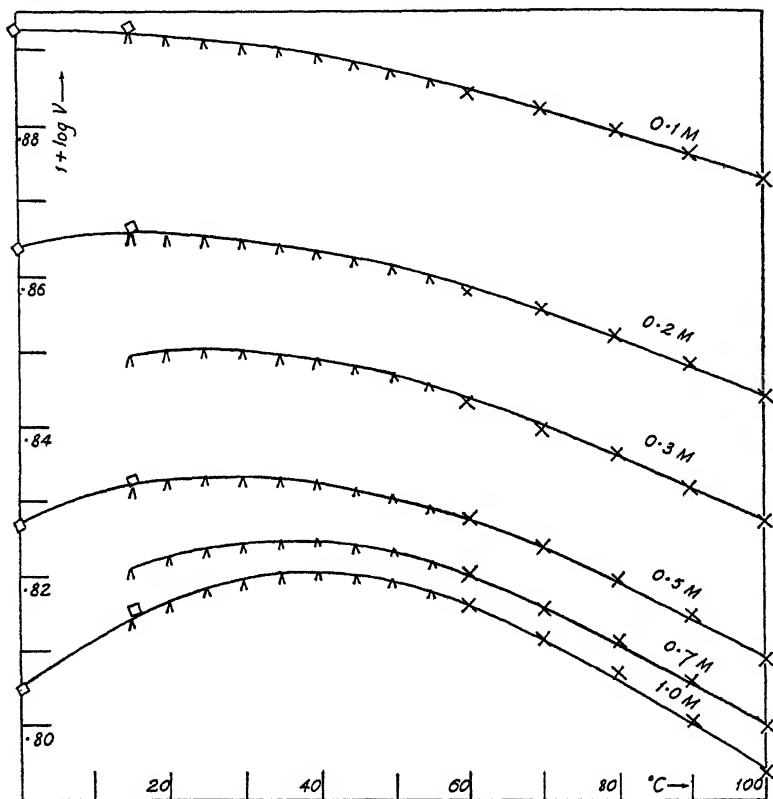


FIG. 1.—Activity coefficient of sodium chloride; 0.1 to 1.0 M., between 0° and 100°.

- ◇ E.m.f. measurements of Harned and Nims.
- △ Isopiestic data.
- × Boiling-point measurements of Smith.

using (a) isopiestic data and (b) the e.m.f. data.^{3' 4' 9} In Table II R refers to the isopiestic data and H to the e.m.f. data.

At 15° the agreement is satisfactory at all concentrations. At 40° the agreement is equally satisfactory up to 3 M. NaCl, but at 3 and 4 M. NaCl there are appreciable deviations.

Secondly in Figs. 1 and 2 I have compared γ_{NaCl} between 0° and 100°, using e.m.f. results at 0°, 15°, and 40° isopiestic data between 15° and 60°, and boiling-point measurements between 60° and 100°. The agreement between these three independent measurements is excellent in the concentration range, 0.1 to 1 M. Thirdly, it is possible to use these

TABLE II.—COMPARISON OF THE RATIO $\gamma_{\text{NaCl}}/\gamma_{\text{KCl}}$ AT 15° AND 40°.

m.	0.1.	0.2.	0.5.	1.0.	2.0.	3.0.	4.0.
15°	R. 1.011 H. 1.015	1.022 1.023	1.047 1.046	1.082 1.088	1.160 1.164	1.251 1.253	1.357 1.359
40°	R. 1.012 H. 1.010	1.022 1.021	1.049 1.047	1.087 1.086	1.166 1.164	1.254 1.265	1.357 1.366

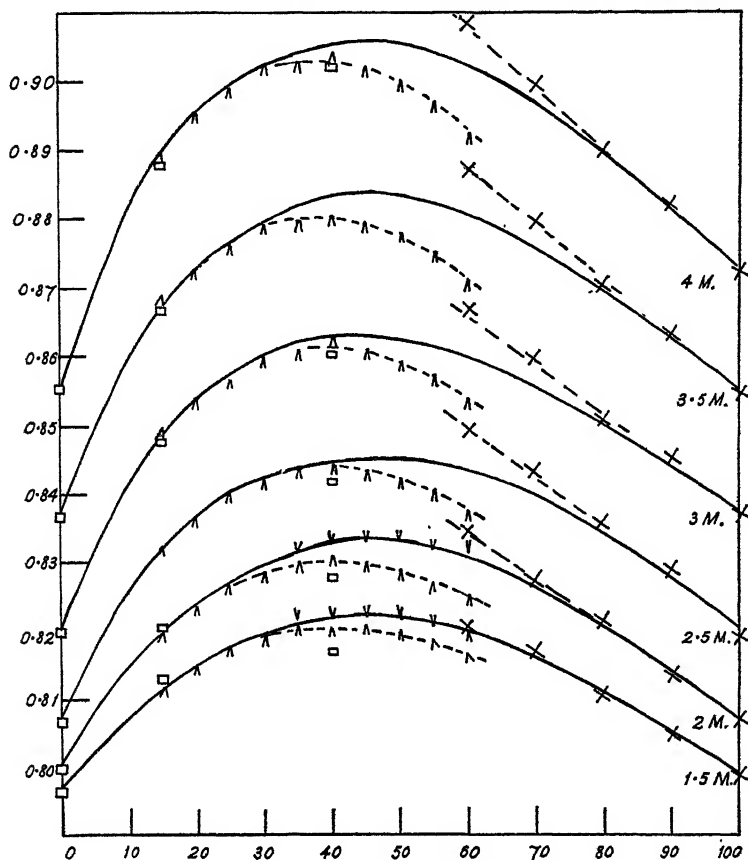


FIG. 2.—The activity coefficients of sodium chloride between 0° and 100° and 1.5 and 4 M.

- E.m.f. data of Harned and Nims.
 △ Isopiestic data.
 × Boiling-point data of Smith and Hirtle.

The dotted curves between 30° and 60° are drawn through the isopiestic data, those above 60° through the boiling-point data. The full curves represent the best that can be drawn through all the points. At 1.5 and 2 M. the thermal data of Rossini for potassium chloride give a second set of data from the isopiestic results between 30° and 60°. These lie on the upper curves.

activity coefficients to calculate the partial molal heat content of sodium chloride in terms of the heat content at 25°, the partial molal heat capacity and the temperature coefficient of the latter, *i.e.*, from the integration of $d \ln \gamma/dT = -\bar{L}_2/2RT^2$ where

$$\begin{aligned}\bar{L}_2 &= \bar{L}_2^{25} + \alpha(t - 25) + \beta(t - 25)^2, \\ \bar{L}_2^{25} &= \text{partial molal heat content at } 25^\circ, \\ \alpha &= \text{partial molal heat capacity at } 25^\circ, \text{ both relative} \\ &\quad \text{to infinite dilution.} \\ 2\beta &= \text{temperature coefficient of the heat capacity.}\end{aligned}$$

We have results available at temperatures between 0° and 100° and it would be possible to use the method of "least squares" to obtain best values of \bar{L}_2^{25} , α and β . For a preliminary calculation, however, I have selected values of γ_{NaCl} at four spaced temperatures, *i.e.*, 0°, 25°, 60°, and 100°, and solved the three simultaneous equations of the form $\ln \gamma^{25}/\gamma = f(t, \bar{L}_2^{25}, \alpha, \beta)$ for \bar{L}_2^{25} , α and β . I used the data of Harned and Nims at 0° the isopiestic results at 25° and 60°, and the, data of Smith at 100°. The thermal data are recorded in Table III.

TABLE III.—PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF SODIUM CHLORIDE.

<i>m</i>	\bar{L}_2^{25}			α		β
	R	G	Y	R	G	R
0.1	95	99.6	94	4.5	5	0.003
0.2	70	85.0	78	5.7	7.1	.013
0.3	35	62	50	7.4	—	.015
0.5	-31	-4	-19	10.3	11.2	.015
0.7	-117	-87	-85	11.9	—	.020
1.0	-191	-188	-186	14.1	15.6	.028

The heat contents under R were obtained from the isopiestic data; those under G were taken from the results of Gulbranson and A. L. Robinson^{6, 7} (the values at 0.3, 0.5, and 0.7 *m*. by graphical interpolation); similarly those under Y were taken from the results of Young and Vogel.⁸ All the heat content results from isopiestic data are within 30 cal. of the direct measurements and this is the error which Harned and Cook anticipate in such results deduced from e.m.f. data. The partial molal heat capacities agree well with the data of Gulbranson and Robinson; they are, however, considerably lower than the results of Rossini. My heat capacity data fit the equation: $\alpha = 14.1 \sqrt{m}$; Gulbranson and Robinson obtained a slope of 15.8.

A reference to Fig. 2 shows that there are two curves possible for γ_{NaCl} at 1.5 and 2 *m*. between 30° and 60°, a higher curve resulting if use is made of the thermal data of Rossini to calculate the activity coefficient of the reference salt, potassium chloride. The lower curve results if the thermal data of Harned and Cook are used to extrapolate γ_{KCl} to 60°.

Smith and Hirtle¹¹ have extended the boiling-point method to concentrations between 1.5 and 4 *m*. — NaCl and temperatures between

¹¹ *J. Amer. Chem. Soc.*, 1939, 61, 1123.

60° and 100°. In their paper they point out that the e.m.f. determinations of Harned and Nims yield low values of the activity coefficient at 40° while the boiling-point method appears to work most accurately at 80°, 90° and 100°, yielding high values of the activity coefficient at 60° and, to a lesser extent, at 70°. This is illustrated in Fig. 2 which shows that a smooth curve can only be obtained by tracing the curve above the e.m.f. point at 40° and below the boiling-point data at 60° and 70°. It follows that the isopiestic data are also low between 35° and 60° and the cause of this discrepancy is probably to be found in the use of the heat content and heat capacity data for potassium chloride obtained by Harned and Cook. As the e.m.f. data for sodium chloride yield low activity coefficients at 40°, it is justifiable to suspect that this is also true for potassium chloride. It is therefore possible that all the activity coefficients used for potassium chloride above 1 M. and between 35° and 60° are low and in this case the results calculated for sodium chloride by the isopiestic method will also be low. Support for this point of view is obtained from the data for sodium chloride at 1.5 and 2 M. using the thermal data of Rossini to calculate the activity coefficient of potassium chloride. These are higher than the data of Harned and Cook and therefore yield higher values of γ_{NaCl} which interpolate very satisfactorily between the boiling-point results and the e.m.f. data at 0°, 15° and 25°.

As the e.m.f. data for sodium chloride at 0°, 15° and 25° and the boiling-point data at 80°, 90° and 100° may be considered very reliable I have used the values at 0°, 25°, 80° and 100° to calculate the following thermal data for sodium chloride, the partial molal heat content under G being taken for comparison from the data of Gulbranson and Robinson (Table IV).

With the aid of these thermal quantities I calculated γ_{NaCl} between 35° and 60° and found the values given in Table V. These lie on the full curves of Fig. 2. These may be taken as the best compromise available between the e.m.f. and boiling-point data.

TABLE V.—ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE ABOVE 1 M. AND BETWEEN 15° AND 60°.

m.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
1.5	0.648	0.654	0.657	0.660	0.662	0.664	0.662	0.662	0.660	0.658
2	.660	.667	.671	.674	.678	.680	.682	.680	.679	.677
2.5	.680	.687	.692	.695	.701	.704	.705	.705	.704	.701
3	.707	.715	.720	.725	.729	.731	.732	.731	.729	.726
3.5	.740	.746	.752	.758	.763	.765	.766	.765	.764	.761
4	.777	.787	.793	.799	.805	.807	.808	.807	.804	.801

Using the isopiestic data I now found what values of the activity coefficient of potassium chloride above 35° would be consistent with these

TABLE IV.

	\bar{L}_2^{25} .		α .	β .
m	R	G		
1.5	— 345	— 343	21.2	— 0.080
2	— 486	— 466	23.6	— 0.039
2.5	— 615	— 556	28.3	— 0.049
3	— 630	— 626	35.3	— 0.197
3.5	— 680	— 671	35.8	— 0.167
4	— 733	— 688	41.5	— 0.211

values of γ_{NaCl} . At 40° these values of γ_{KCl} must be between 0.003 and 0.009 higher than those recorded by Harned and Cook. At all concentrations above 1 M. the curve of γ against temperature passes through a very flat maximum at 45°. It will serve no purpose to record all the data for potassium chloride but the following figures enable a satisfactory curve to be reconstructed:—

<i>M</i> — KCl.	1.5.	2.	2.5.	3.	3.5.	4.	4.5.
γ at 45°	0.588	0.583	0.582	0.584	0.587	0.595	0.604
γ at 60°	.582	.578	.578	.580	.584	.591	.600

The thermal data for potassium chloride, corresponding to these figures are given in Table VI.

TABLE VI.

<i>m.</i>	\bar{L}_2^{25} .	α .	β .
1.5	— 263	19.3	+ .006
2	— 384	21.9	— .044
2.5	— 493	23.6	+ .043
3	— 561	27.2	— .035
3.5	— 598	27.5	+ .049
4	— 668	29.2	+ .077

Summary.

The isopiestic ratio of potassium and sodium chloride has been measured over the concentration range 0.1 — 4 M. NaCl at 5° intervals between 15° and 60°.

For concentrations of 1 M. or less the activity coefficients of sodium chloride form a link between similar results obtained by Harned and Nims from e.m.f. measurements at lower temperatures and those obtained by Smith from boiling-point measurements at high temperatures. The iso-piestic

results interpolate very satisfactorily. Over this concentration range a large amount of work can be shown to be self-consistent, *viz.*, the e.m.f. work of Harned and Nims on sodium chloride and of Harned and Cook on potassium chloride, the isopiestic data, the boiling-point results of Smith and the partial molal heat contents and heat capacities obtained by Gulbranson and Robinson and by Young and Vogel.

For concentrations above 1 M. similar concordance can be obtained provided that it is assumed that the e.m.f. measurements give low activity coefficients of both sodium and potassium chloride at 45°. With this assumption the e.m.f. data up to 30°, the isopiestic results and the boiling-point experiments of Smith and Hirtle become self-consistent. The rejection of the e.m.f. data at 40° invalidates previous calculations of thermal data at high concentrations; a full statistical analysis of this mass of results will have to be made, but an approximate calculation has been made of the heat content and heat capacity of each salt from activity coefficient data at four spaced temperatures. In the case of sodium chloride good agreement obtains with the direct calorimetric measurements of the partial molal heat content. In the case of potassium chloride no such comparison is possible but in both cases the effect of these considerations is to lower the heat content data calculated from e.m.f. results by 100-200 cal. and also to lower the heat capacity data.

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THE ACTIVITY COEFFICIENTS OF SULPHURIC ACID AND LANTHANUM CHLORIDE IN AQUEOUS SOLUTION AT 25°.

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The activity coefficients of sulphuric acid and of lanthanum chloride have been determined as part of a study of electrolytes in aqueous solution and as neither can be grouped in any well-defined category of electrolytes, it seems desirable to report upon them separately. Sulphuric acid is of interest in itself because of its common use, whilst lanthanum chloride is one of the few univalent salts which can readily be obtained in a pure state and do not undergo hydrolysis in solution.

Sulphuric Acid.

In determining the isotonic or isopiestic ratio between this electrolyte and potassium chloride, the acid was contained in platinum crucibles sunk into holes in a copper block, the potassium chloride being contained in the silver dishes normally employed in this method. The platinum crucibles did not fit into the copper block as well as could be desired, and for this reason the measurements were not carried below 0.2 M. H_2SO_4 . The available measurements enable the activity coefficient to be calculated between 0.2 and 3 M. H_2SO_4 . The following pairs of solutions were found to be isopiestic, the molality of potassium chloride being given first in each case:

0.2140, 0.1946;	0.2434, 0.2213;	0.3885, 0.3495;	0.4036, 0.3614;	0.5446, 0.4832;
0.6647, 0.5833;	0.7268, 0.6376;	0.8200, 0.7101;	0.8702, 0.7492;	0.9245, 0.7908;
1.022, 0.8666;	1.075, 0.9068;	1.176, 0.9788;	1.226, 1.015;	1.238, 1.024;
1.275, 1.051;	1.413, 1.151;	1.468, 1.185;	1.654, 1.316;	1.728, 1.368;
1.858, 1.456;	2.048, 1.575;	2.119, 1.627;	2.367, 1.776;	2.522, 1.873;
2.524, 1.873;	2.652, 1.951;	2.916, 2.108;	2.937, 2.127;	3.066, 2.203;
3.221, 2.283;	3.252, 2.302;	3.270, 2.308;	3.450, 2.412;	3.451, 2.412;
3.557, 2.476;	3.623, 2.518;	3.678, 2.544;	3.846, 2.629;	3.863, 2.639;
3.864, 2.641;	3.925, 2.663;	3.989, 2.696;	4.010, 2.711;	4.087, 2.757;
4.116, 2.777;	4.171, 2.800;	4.293, 2.866;	4.310, 2.867;	4.610, 3.024;
4.629, 3.032;	4.810, 3.120;	4.841, 3.136.		

Using these figures, the isopiestic ratio ($3m_{H_2SO_4}/2m_{KCl}$) against $m_{H_2SO_4}$ was plotted and values read off at round concentrations. Using the activity coefficients of potassium chloride given by Scatchard, Hamer and Wood,¹ $\gamma_{H_2SO_4}$ was calculated in order that a comparison could be made between my isopiestic data and the isopiestic determination made independently by these workers on sulphuric acid—potassium chloride. The agreement was excellent as can be seen from the following comparison at a few concentrations:

	<i>m.</i>	0.5	1.0	1.4	2.0	2.5	3.0
$1 + \log \lambda$	{ Robinson	0.1913	0.1198	0.0995	0.1031	0.1225	0.1542
	{ S. H. and W.	0.1931	0.1181	0.0997	0.1034	0.1229	0.1525

¹ *J. Amer. Chem. Soc.*, 1938, 60, 3061.

In both cases the activity coefficients are based on the value $1 + \log \gamma = 0.3202$ at 0.2 M. H_2SO_4 . The mean deviation between the two determinations is 0.2 per cent. of the activity coefficient. This comparison is an excellent test of the reproducibility of results obtained by the isopiestic method by independent work in different laboratories.

In an earlier paper,² however, it has been shown that the e.m.f. data on some alkali halides can be reconciled with the isopiestic data by taking a set of reference values for γ_{KCl} which are considerably higher above 1.5 M. KCl than those adopted by Scatchard, Hamer and Wood. The discrepancy is largely due to the greater emphasis I have placed on the e.m.f. results, and until a direct determination of the osmotic or activity coefficient of potassium chloride is made by another method, both sets of reference values for γ_{KCl} must be regarded as equally probable. To be consistent, as a considerable number of results have previously been referred to the standard for γ_{KCl} , this standard must be adopted in calculating $\gamma_{\text{H}_2\text{SO}_4}$, thereby obtaining a set of activity coefficients for sulphuric acid which will differ from those of Scatchard, Hamer and Wood, in the same way as the coefficients for potassium chloride differ. The two sets of values for $\gamma_{\text{H}_2\text{SO}_4}$ must be regarded as equally probable until the values of γ_{KCl} are ascertained with certainty. The data based on my values for γ_{KCl} are as follows:

m	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$1 + \log \gamma$	0.3169	0.2589	0.2174	0.1981	0.1656	0.1482	0.1350	0.1247
m	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
$1 + \log \gamma$	0.1166	0.1046	0.0963	0.0949	0.0965	0.0999	0.1064	0.1135
m	2.6	2.8	3.0					
$1 + \log \gamma$	0.1247	0.1372	0.1510					

As the extrapolation of the isopiestic ratio cannot be carried back from 0.2 M. H_2SO_4 to infinite dilution an arbitrary value of $\gamma_{\text{H}_2\text{SO}_4} = 0.207$ at 0.2 M. H_2SO_4 has been adopted, a value which best fits the data with which comparison is possible.

Table I compares these activity coefficients with three other sets which have been obtained from e.m.f. measurements by Harned and Hamer,³ Randall and Cushman⁴ and MacDougall and Blumer⁵; these are referred to as (1) (2) and (3) respectively in the table. In calculating the activity coefficient from an e.m.f. measurement, the value of $E_0 = 0.61515$ given by Harned and Hamer has been used.

TABLE I.—COMPARISON OF ACTIVITY COEFFICIENT OF SULPHURIC ACID.

m	0.2	0.28	0.5	0.56	0.85	1.0
γ { Isopiestic	0.207	0.186	0.154	0.149	0.135	0.131
γ { E.M.F.	0.209 (1)	0.186 (2)	0.154 (1)	0.150 (2)	0.134 (2)	0.130 (1)
		0.187 (3)		0.150 (3)		
m	1.133	1.141	1.5	1.717	1.752	2.0
γ { Isopiestic	0.128	0.128	0.125	0.125	0.125	0.126
γ { E.M.F.	0.127 (2)	0.129 (3)	0.124 (1)	0.124 (2)	0.126 (3)	0.125 (1)
m	2.313	2.387	2.922	3.0		
γ { Isopiestic	0.129	0.130	0.140	0.142		
γ { E.M.F.	0.128 (2)	0.132 (3)	0.141 (2)	0.141 (1)		

² *Trans. Faraday Soc.*, 1939, **35**, 1217.

³ *J. Amer. Chem. Soc.*, 1935, **57**, 27.

⁴ *Ibid.*, 1918, **40**, 393; *I.C.T.*, VI, 323.

⁵ *Ibid.*, 1933, **50**, 2236.

Grollman and Frazer⁶ have made a direct vapour pressure determination on sulphuric acid from which they calculated activity coefficients. Considerable difficulty is experienced in finding a reference value for these coefficients, and as the data given by Grollmann and Frazer are uniformly higher than those of other workers, there can be no doubt that they selected too high a reference value. Nevertheless, the curve of their activity coefficients should be parallel to the correct curve. I find that the data of Grollman and Frazer are higher than mine by a mean amount of 0.0584 in $\log \gamma$, the differences lying between 0.0542 and 0.0612. The agreement with the results of Grollman and Frazer is therefore, as good as that with e.m.f. data. Taking both the e.m.f. data and the vapour pressure results into consideration, it is found that, with the exception of one result where there is a difference of 2 per cent. in γ , the isopiestic results never differ from the others by as much as 1 per cent. A curve drawn through my activity coefficients for sulphuric acid may therefore be taken as a good representation of all the results which have been obtained on this electrolyte.

Lanthanum Chloride.

The activity coefficient of this salt has been determined independently by Robinson⁷ and by Mason⁸ using the isopiestic method, and by Shedlovsky and MacInnes⁹ who used cells with transport. The latter method gave the activity coefficient up to a concentration of 0.0333 mol. per litre although the equation given by Shedlovsky and MacInnes for $\log \gamma$ in terms of m is probably valid up to 0.05. The isopiestic method has been used from concentrations of 0.05 M. upwards. Excellent results have been obtained in concentrated solutions, but if the isopiestic data are plotted as isopiestic ratios ($m_{\text{KCl}}/2m_{\text{LaCl}_3}$) against m_{LaCl_3} or better $\sqrt{m_{\text{LaCl}_3}}$, it becomes evident that the curve is not well-defined between 0.05 and 0.2 M. Moreover, when the isopiestic data were originally determined, there was some difficulty in assigning a value to the activity coefficient at the lowest concentration, the values at other concentrations being calculated relative to this. Robinson used the value for lanthanum nitrate, $\gamma = 0.380$, at 0.05 M.; Mason used the extended Debye-Hückel equation to extrapolate his results to infinite dilution and obtained $\gamma = 0.162$. The equation of Shedlovsky and MacInnes leads to $\gamma = 0.447$ at 0.05 M. and an examination of their data up to 0.03 M., plotted as $\log \gamma$ against \sqrt{m} , shows that even if their equation is not valid up to 0.05 M., nevertheless, γ at 0.05 M. must be considerably higher than the values assigned by either Mason or Robinson. It only remains, therefore, to bridge this gap between approximately 0.033 and 0.2 M. to complete the activity coefficient data up to 1.5 M.

The isopiestic data have now been supplemented by a few more determinations as follows, the concentration of potassium chloride being given as the first of each pair of figures :

0.2348, 0.1351; 0.2957, 0.1690; 0.3602, 0.2025; 0.3871, 0.2155;
 0.4035, 0.2246; 0.8344, 0.4239; 0.9745, 0.4828; 1.160, 0.5556;
 1.168, 0.5602; 1.699, 0.7490; 2.313, 0.9458; 2.482, 0.9982;
 2.804, 1.086; 3.197, 1.188; 4.518, 1.512.

From the combined isopiestic data, activity coefficients can be calculated accurately from 0.2 M. upwards relative to an arbitrary value at any one concentration and less accurately between 0.1 and 0.2 M. The

⁶ *J. Amer. Chem. Soc.*, 1925, 47, 712.

⁸ *Ibid.*, 1938, 60, 1638.

⁷ *Ibid.*, 1937, 59, 84.

⁹ *Ibid.*, 1939, 61, 200.

portion of the curve (Fig. 1) up to A corresponds to the data of Shedlovsky and MacInnes. Because of the arbitrary value assigned to γ at 0.2 M. the portion of the curve obtained from the isopiestic data, BC, can be moved up or down parallel to the $\log \gamma$ axis and the problem is to find the position of curve BC which will enable the gap AB to be bridged smoothly. It is clear from Fig. 1 that an attempt to fix γ at 0.2 M. by moving the curve BC until it coincides with a projection from A cannot be successful. The curve BC in Fig. 1 is in the position assigned to it by using another method, but it is clear that the curve could be moved an appreciable distance up and down without interfering with the smoothness of the interpolation between A and B. On the left-hand side of Fig. 1 are plotted the osmotic coefficient data of Shedlovsky and MacInnes together with similar data in more concentrated solutions calculated by Mason from his isopiestic results. An attempt was made to interpolate a smooth curve

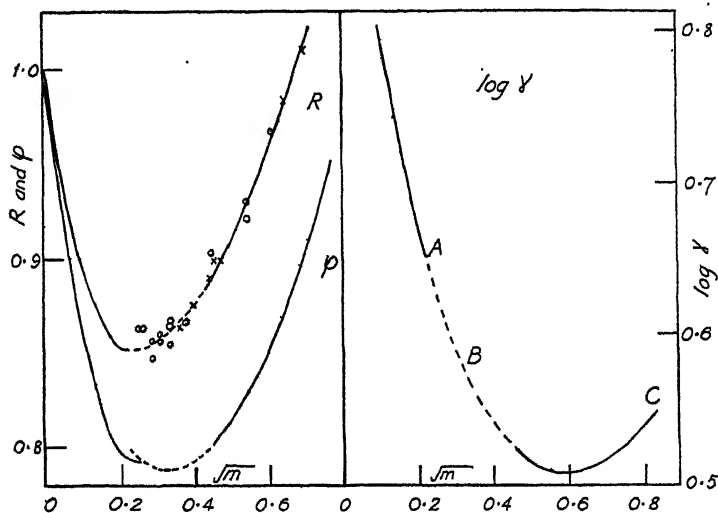


FIG. 1.—The osmotic coefficient (ϕ), isopiestic ratio (R), and activity coefficient (γ) of lanthanum chloride, \odot Mason, \times Robinson.

over the concentration range 0.05–0.2 M., but although the activity coefficients calculated therefrom agreed substantially with those obtained by a third method, there was considerable uncertainty about the exact position of the ϕ curve in this region. However, the following method was found practicable: The osmotic coefficients of lanthanum chloride are given by the equation of Shedlovsky and MacInnes: $\phi_2 = 1 - 1.749 \sqrt{m_2} + 3.673 m_2$. It was also found that the osmotic coefficients of potassium chloride in dilute solution could be expressed as

$$\phi_1 = 1 - 0.3757 \sqrt{m_1} + 0.4757 m_1,$$

using the data of Shedlovsky and MacInnes.¹⁰

The condition that the two solutions shall be isopiestic is:

$$2m_2\phi_2 = m_1\phi_1,$$

or $R - 0.5311 \sqrt{m_2} R^{3/2} + 0.9514 m_2 R^2 = 1 - 1.749 \sqrt{m_2} + 3.673 m_2$ where the isopiestic ratio, $R = m_1/2m_2$.

This equation gives the isopiestic ratio corresponding to the e.m.f. measurement of Shedlovsky and MacInnes on lanthanum and potassium

¹⁰ J. Amer. Chem. Soc., 1937, 59, 503.

chloride, and should be valid up to 0.05 M. LaCl_3 . It yields the following isopiestic ratios :

m_2	.	.	0.01	0.025	0.04	0.05
R	.	.	0.900	0.865	0.853	0.852

If a curve of R is plotted against $\sqrt{m_2}$ (Fig. 1) utilising both the data calculated for concentration up to 0.05 M. and the results determined above 0.05 M., it is easy to interpolate the correct curve between 0.05 and 0.2 M. in spite of a considerable scattering of the experimental points in this region. The determination of the activity coefficient over the whole concentration range is then only a matter of computation; they are given in Table II. The activity coefficient of potassium chloride above 0.1 M., which is necessary for the calculation, has been given by Robinson.²

TABLE II.—ACTIVITY COEFFICIENTS OF LANTHANUM CHLORIDE AT 25°.

m	.	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7
		0.447	0.383	0.337	0.323	0.322	0.328	0.338	0.354
m	.	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
		0.373	0.396	0.424	0.456	0.493	0.536	0.587	0.647

Shedlovsky and MacInnes have shown that the limiting slope of $\log \gamma$ against \sqrt{m} does not agree with the Debye slope even in the most dilute region and that their results are not concordant with ion-pair formation or incomplete dissociation of the salt. Consequently, no useful purpose would be served by discussing the application of the extended Debye-Hückel equation to the concentrated solution.

Summary.

The activity coefficient of sulphuric acid has been determined by the isopiestic method at 25° between 0.2 and 3 M.; the results are in good agreement with e.m.f. and direct vapour pressure determinations and the results quoted may be taken as a good representation not only of the isopiestic results, but also of the other measurements.

The activity coefficient of lanthanum chloride has been ascertained up to 1.5 M. from a consideration of isopiestic data and the e.m.f. of cells with transport.

I am indebted to the Chemical Society for a grant from the Research Fund which has assisted these investigations.

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CONTRIBUTIONS TO THE GENERAL CHEMISTRY OF COLLOID-COLLOID REACTIONS. VII.*

HIGHLY PURIFIED PROTECTED Sb_2S_3 SOLS.†

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Preliminary experiments showed that electrodecantation (E.Dec.) of a mixture of a highly purified antimony trisulphide sol and a highly purified dextrin sol gives, after repeated replacements of the top layer with conductivity water, a dextrin-free top layer. This method provided for the first time the protected and highly purified sols, the structure of which we have studied.

The respective proportions of Sb_2S_3 and dextrin when the latter is present only in small quantities were determined by boiling the protected sols with concentrated HCl. The glucose formed was determined gravimetrically, using Fehling's solution. A dextrin-free Sb_2S_3 sol, after boiling with HCl until no H_2S is left, does not reduce the Fehling's solution, although Sb^{+++} is present. No Cu_2O is formed even after several weeks. Under similar conditions Trommers' solution gives a Cu_2O precipitate after boiling for two hours.

Sufficient concentrated HCl was added to dissolve the Sb_2S_3 on boiling, the H_2S boiled off and the solution, when cold, neutralised with NaOH when $\text{Sb}(\text{OH})_3$ was precipitated. Since glucose becomes resinous when boiled with NaOH, the solution was acidified again until the $\text{Sb}(\text{OH})_3$ was dissolved, boiled and boiling hot Fehlings' solution added. The precipitated Cu_2O was weighed as CuO . Prolonged boiling of the acidic solution is to be avoided because of the decomposition of the glucose, shown by the discoloration of the solution.

We ascertained the smallest possible concentration of glucose which could be determined by Fehling's solution. Bigger quantities could be determined gravimetrically. Small quantities of the order of 5×10^{-4} per cent. could be estimated by comparison of their very distinct Tyndall effect in the light of an arc lamp with that of solutions containing known quantities of dextrin after decomposition by HCl and treatment with Fehling's solution.

The dextrin in the upper layer was detected by means of the deep violet coloration of iodine solution. The limit of sensitivity of the method was about 0.001 g. per litre. When this limit was reached the electrodecantation was once repeated.

Preparation of Highly Purified Mixed Sb_2S_3 -Dextrin Sols.

Table I shows the data for three Sb_2S_3 sols, prepared and characterised by the method published elsewhere.¹

The calculation of the colloid equivalent K' (the amount of Sb_2S_3 molecules corresponding to 1 free charge, i.e., to 1 free H ion, was made

* The previous contribution VI, see Wo. Pauli and W. Kitaj, *Koll. Z.*, 1938, 43, 82.

† The experiments were carried out in the Institute for Medical Colloid Chemistry of the University of Vienna, and were interrupted in spring of 1938.

¹ W. Pauli, W. Kölbl and A. Laub, *Koll. Z.*, 1937 80, 175.

TABLE I.

Sol.	Sb ₂ S ₃ Content (g. per litre).	$M_{Sb_2S_3}$ $\times 10^2$.	$\kappa \times 10^5$.	$H_{\kappa} \times 10^4$, ($u+v=400$).	$H_{titr.} \times 10^4$.		Colloid Equivalent K' .
					1st Break.	2nd Break.	
S ₁	17.3	5.1	21.4	5.4	10.7	26.0	95
S ₂	7.2	2.1	6.16	1.54	—	—	136
S ₃	4.93	1.4	4.68	1.17	1.35	3.71	120

from the value of the hydrogen ion concentration calculated from the conductivity κ . H ion concentration obtained by titration includes a part of the inactivated H⁺.

Dextrin D₃ (Table II) was an acidoid dextrin, having 1 uronic acid group for 10 dextrin particles ($M_D = 6000$) and 1 phosphoric acid group for about 19 dextrin particles.²

TABLE II.

Sol.	g. Per Litre.	M_D $\times 10^3$.	P Per Cent.	$\kappa \times 10^4$.	H_{κ} $\times 10^4$.	a_H^* $\times 10^4$.	c_H^\dagger $\times 10^4$.	Urs. N. $\times 10^4$.	Phos- phoric Acid N. $\times 10^4$.
D ₃	48.5	8.08	0.027	2.07	5.17	5.2	16.46	8.01	8.44

* a_H is the value found by potentiometric measurement.

† c_H is the total concentration of H-ions corresponding to the second break of the titration curve.

The amount of dextrin needed to protect 0.2 c.c. of those sols against KCl of a final concentration 5×10^{-2} N. (threshold value) was as follows: 0.2 c.c. of Sol 1 containing 0.00247 g. Sb₂S₃ were found to be completely

TABLE III.

Electrodecentration.	Dextrin in the Top Layer.	$\kappa \times 10^6$ Top Layer.
1	+	—
2	+	3.34
3	—	4.50
4	—	2.29

of an electrodialyser. An initial potential of 33 V. was applied and the electrodecentration carried out every 3 hours in complete darkness. The top layer was syphoned off and tested for dextrin. Table III shows the progress of the purification. The sol was stored in darkness in "Jena" flasks with a ground glass cap.

The characterisation of these sols was carried out in a manner similar to that of the unprotected sols, and a dextrin determination also made. The concentration was determined by drying at 110° to constant weight.

S_1 , S_2 , and S_3 are the Sb_2S_3 sols, the corresponding protected sols being Sp_1 , Sp_2 and Sp_3 . Table IV gives the data for sols S_1 and Sp_1 .

The active $[\text{H}^+]$ concentration in Sp_1 was (as calculated from κ)

$$K = 1.15 \times 10^{-4} \text{ N.}$$

The corresponding colloid equivalent K' was 217. The initial sol S_1 had shows that a decrease of charge density has taken place. With K' of 95 the corresponding $[\text{H}^+]$ should be $2.5 \times 10^{-4} \text{ N.}$ That corresponding to the dextrin present is about $1.9 \times 10^{-5} \text{ N.}$, indicating that the charge of protected purified sol is provided mainly by the ionogenic groups of the Sb_2S_3 sol and not by those of dextrin.

During electrodecantation the dextrin content decreased from 78.5 to 20 g. dextrin per 100 g. of Sb_2S_3 without the protective action being impaired. The remaining dextrin (approximately one-fourth of the original amount) adheres to the Sb_2S_3 particles of the sol, and does not appear to be in the intermicellar liquid.

0.2 c.c. of sol S_2 (0.00144 g. Sb_2S_3) were completely protected by 0.2 c.c. of ten times diluted dextrin D_3 (0.00097 g.). The sol Sp_2 was prepared by electrodecantation of a mixture of 60 c.c. of the sol S_1 with 60 c.c. of ten times diluted dextrin D_3 . A voltage of 35 V. was applied, and each electrodecantation lasted for about 2 hours. The data of Sp_2 are also given in Table IV.

The pure, protected sol Sp_2 has H_κ of $3.4 \times 10^{-8} \text{ N.}$ which corresponds to K' of 218. This, like the sol Sp_1 , shows a large decrease of the charge density in comparison with the charge of the particles of the initial sol S_2 ($K' = 136$). For the latter $[\text{H}^+]$ of $5.45 \times 10^{-5} \text{ N.}$ was calculated, while the dextrin contained in the sol could provide $2.6 \times 10^{-6} \text{ N.}$ at the most. This small value shows that the dextrin contributes practically nothing to the charge of the protected particles.

The dextrin content which was 53.5 g. per 100 g. of Sb_2S_3 in the initial mixture, dropped to 9.84 per 100; i.e., four-fifths of the added dextrin was removed. The remainder which cannot be removed by further E.Dec. is sufficient to protect the antimony sulphide sol.

The following experiment is of a certain interest. To two separate 60 c.c. portions of sol S_3 different quantities of dextrin were added: to one portion (a) a quantity just sufficient completely to protect it against KCl and to the second (b) a quantity ten times as great. These two

TABLE IV.

Sol.	Content per Litre.		Sb_2S_3 , (10^{-4} m.)	κ .		H_{littr}		K' .	Threshold Value N. KCl.	
	Sb_2S_3 .	Dextrin.		Top Layer.	Sol.	1st Break.	2nd Break.		Turbidity.	Coagulation.
S_1	17.3	—	5.1	3.7×10^{-6}	2.14×10^{-4}	1.07×10^{-3}	2.6×10^{-3}	95	3×10^{-2}	5×10^{-2}
Sp_1	8.75	1.75	2.45	3	4.57×10^{-5}	2.61×10^{-4}	8.1×10^{-4}	217	—	8×10^{-2}
S_2	7.2	—	2.1	4.3×10^{-6}	6.16×10^{-5}	—	—	136	3×10^{-2}	5×10^{-2}
Sp_2	2.549	0.251	0.7	2.3×10^{-6}	1.36×10^{-5}	3.6×10^{-5}	—	218	7×10^{-2}	8×10^{-2}

mixed sols were both diluted to 800 c.c. each with conductivity water and electro dialysed in two similar electro dialysers with a starting voltage of 37 V. Table V shows the progress of the removal of dextrin and the

TABLE V.

Sol a.			Sol b.		
E. Decan- tation.	Dextrin in Top Layer.	Top κ Layer.	E. Decan- tation.	Dextrin in Top Layer.	Top κ Layer.
1	+	2.92×10^{-6}	1	very much	7.2×10^{-6}
2	?	2.3×10^{-6}	2	+	2.95×10^{-6}
3	—	2.8×10^{-6}	3	little	2.69×10^{-6}
4	—	2.32×10^{-6}	4	—	2.61×10^{-6}
			5	—	2.35×10^{-6}

composition of the resulting protected sols. The time of removal of dextrin was longer for the portion (b). Both final purified sols had preserved the protective power of the starting mixtures. Table VI gives the data of the sols.

TABLE VI.

Sol.	Content per Litre.		$M_{Sb_2S_3}$	κ .		$H_\kappa \times 10^5$.	K' .
	Sb_2S_3 .	Dextrin.		Top Layer.	Sol.		
S_3	4.93	0	14×10^{-3}	—	4.68×10^{-5}	11.7	120
Sp_3a	2.585	0.845	7.6×10^{-3}	2.32×10^{-6}	2.22×10^{-5}	5.55	137
Sp_3b	1.98	0.75	5.8×10^{-3}	2.35×10^{-6}	1.57×10^{-5}	2.76	210

In the initial sol S_3 H_κ , as in the previous experiments, is greater for the same Sb_2S_3 content as in both Sp_3a and Sp_3b . The calculated H_κ for sol Sp_3a is 5.55×10^{-5} N., against 6.46×10^{-5} N. for sol S_3 . Sol Sp_3b gives H_κ of 2.76×10^{-5} N., when for the same concentration of S_3 one should have $H_\kappa = 3.9 \times 10^{-5}$ N. The acidity from dextrin cannot be greater than 8 to 9×10^{-6} N. It is therefore clear that the charge is provided by the ionogenic complexes of the Sb_2S_3 particles. Sol Sp_3b , which was prepared by the addition of ten times as much dextrin, has 30 g. dextrin per 100 g. Sb_2S_3 as against 33 % in the sol Sp_3a . This slight difference is perhaps due to experimental error in the dextrin determination. In any case it is very small in comparison with the composition of the starting mixtures.

Review of the Results.

Electrodecanatation of a mixture of purified and characterised Sb_2S_3 sols with an equally purified acidoid dextrin sol, gives pure mixed protected sols, free from excess of dextrin. This excess can attain $3/4$ to $4/5$ of the dextrin needed for complete protection against KCl of the

initial Sb_2S_3 sol in the flocculation tubes. The rest of the dextrin remains on the Sb_2S_3 sol particles and is sufficient to maintain the protective action. This protective action implies that there will be a considerable increase of the electrolyte concentration before initial turbidity and complete coagulation set in. At least a certain part of the surface of the particles of the lyophobic sol must be covered with dextrin.

On the other hand, these protected sols show a considerable charge, as shown by both the H^+ titration ($H_{\text{titr.}}$) as well as by the calculated value (H_K) of the H ion concentration, which originate almost completely in the ionogenic complexes of the Sb_2S_3 sol. The charge contributed by the dextrin could not possibly be greater than about 10 % of the values determined. The surface of the particles is covered by dextrin, only to such an extent as partially to prevent the dissociation of the charging complexes. The decrease of the charge density of the protected sols as compared with the initial sols, after the decantation, is in the region of 50 % or somewhat more (for the same Sb_2S_3 content). At first it might be thought that a decrease in the activity of the *Gegenionen* takes place without a change in the total concentration. Determination of the protected sol Sp_1 showed, however, that not only the activity of the H ions but also the total $[\text{H}^+]$ had been decreased numerically from $14 \times 10^{-4} \text{ N.}$ to $8 \times 10^{-4} \text{ N.}$ (calculated from the second break in the ascending portion of the curve).

The question arises, therefore, whether the decrease in charge is caused by the removal of the ionogenic group during the electrodecantation or by the partial covering and screening of the surface of the particles by a dextrin layer. Our observations seem to show that the latter is the case. This is substantiated by the fact that the conductivity values of the top layer during the E.Dec. are rather small. If there were eliminated with the top layer not only dextrin but also a part (say half) of the ionogenic complexes, its conductivity would be much larger. Such increased values of the conductivity of the top layer are observed for example in the case of Fe_2O_3 and Al_2O_3 sols, which lose their ionogenic complexes by hydrolysis during E.Dec.

Our observations seem to be consistent with the assumption that the acidoid dextrin covers the particles of the pure Sb_2S_3 sols with a coarsely porous or finely meshed film. This allows a certain ionisation, but at the same time hinders the free access of the *Gegenionen*, which must have a larger diffusion potential in order to pass this shell and become deactivated. The protected sol remains electrocratic, in other words, it is stable by virtue of its electrostatic charge. The disappearance of about 50 % of the total charge seems to suggest that about half of the particle surface remains accessible to reaction. W. Pauli and Kitaj³ have observed that the protection of a Sb_2S_3 sol increases with increased dextrin concentration. The protective action against high concentrations of salts is, however, never complete. Invariably a turbidity is formed, showing that the dextrin only prevents the formation of a proper flocculation. The increased protective action of the excess of dextrin over and above the quantity adhering to the surface (which was determined in our experiments) is possibly due to the formation of a looser, enlarged shell and to a steric hindrance, produced by the dextrin particles in the medium.

It was assumed³ that the adherence of the electro-negative dextrin to the surface of the negative Sb_2S_3 sol particles is due to the co-

³ W. Pauli and W. Kitaj, *Koll. Z.*, 1938, 82, 43.

ordination of monose links in the carbohydrate to the metallic atoms of the neutral heteropolar surface groups, analogous to the glycol and sugar compounds of metallic salts.⁴ This together with the comparatively low molecular weight of the dextrin ($M = 6000$) would explain the less compact character of the dextrin adherence, as in this case we have no interionic forces.

In the case of electropositive highly purified Fe_2O_3 sol the dextrin has a fully protective action even against high KCl concentrations (2 N.), due probably to the reciprocal electrostatic action, which makes the dextrin film stronger and more compact.

All these experiments agree with simultaneous further elaborated observations on highly purified protected gold sols.⁵

Summary.

1. Mixtures of purified Sb_2S_3 sols and purified acidoid dextrin sols can be purified by electrodecantation until the top layer is free from dextrin.

2. Only a small amount of the added dextrin remains fixed on the sol particles, but this is sufficient to preserve the initial protective power.

3. The surface of the particles of the purified protected sol has the electrochemical constitution of the pure Sb_2S_3 sol, but the charge is reduced to a half.

4. All the properties of the purified protected sol harmonise with the assumption that the particles are covered with a porous or netlike film of dextrin.

⁴ A. Grün and Bockisch, *Ber.*, 1908, 41, 3645; A. Grün and Boedecker, *Ber.*, 1910, 43, 1051; Confer, P. Pfeiffer, *Organ. Molekülverbindungen*, Stuttgart, 1922.

⁵ W. Pauli, J. and St. Szper, in this vol., p. 1178.

SOME NEW OBSERVATIONS ON HYDRAZINE.

By C. H. BAMFORD.

Received 7th June, 1939.

In a previous paper¹ it has been shown that NH_2 and N_2H_3 radicals react readily with nitric oxide. It was decided to utilise these reactions to attempt to determine the nature of the thermal decomposition of hydrazine, a process shown by Askey² to be heterogeneous in a quartz vessel. In a preliminary experiment, using a long quartz reaction vessel, without any special precaution to ensure uniform heating, it was found that mixtures of hydrazine and nitric oxide exploded on heating. On repeating the experiment with smaller pressures of nitric oxide the same result was obtained, and finally, hydrazine itself was shown to explode under the same conditions. If a uniformly heated vessel was employed no explosion occurred, but the hydrazine decomposed on the surface, as found by Askey.

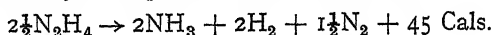
A further experiment was then tried in which a reaction vessel carrying tungsten electrodes was used, the whole being maintained at about 100° . The interesting result was obtained that pure hydrazine vapour explodes when sparked, a yellow flame accompanying the decomposition. This

¹ Bamford, *Trans. Faraday Soc.*, 1939, 35, 568.

² Askey, *J. Amer. Chem. Soc.*, 1930, 52, 970.

property of hydrazine does not appear to have been noticed before, although it is well known that explosions are liable to occur during the preparation of the compound.

The products of the explosion are ammonia, hydrogen and nitrogen, the ammonia and hydrogen being approximately equivalent. The overall reaction may be expressed by the equation :



(taking the values of the N—N, N≡N, N—H, and H—H links as 32, 186, 90, 103 Cals./gm. mol. respectively). The explosion is subject to the usual upper and lower kinetic limits. A brief study of the kinetics of the explosive reaction and of the slow thermal decomposition (heterogeneous) in the presence of nitric oxide are given in the following pages and tentative mechanisms are suggested.

Experimental.

Apparatus. For the study of the heterogeneous decomposition of hydrazine in the presence of nitric oxide a quartz reaction vessel length 10 cm. diameter 3.5 cm. was used. This was surrounded by an electric furnace, which gave a temperature uniform over the length of the reaction vessel to the extent of 1° C. The vessel was in communication with a mercury seal of the type described in a previous paper : the seal could also be used as a constant volume manometer. The reaction vessel carried a side arm which could be cooled in liquid air, in order to distil in the hydrazine *in vacuo*. When the reactant had been introduced into the reaction vessel, the latter was isolated from the remainder of the apparatus by raising the mercury in the seal. The whole of the connecting tubing between the reaction vessel and the mercury seal was maintained at about 100°, by wrapping it with nichrome wire carrying a small current. The upper portion of the mercury column connected to the reaction vessel was also heated to the same temperature. This was necessary in order to obtain sufficient pressures of hydrazine, the vapour pressure at room temperatures being only about 10 mm. The exit tube of the mercury seal communicated with two liquid air traps and a Toepler pump; which were used for fractionating and pumping off the products. The whole apparatus could be exhausted by a mercury diffusion pump and a Hyvac.

The products were separated according to their volatility : by cooling the traps in liquid air, nitrogen and hydrogen could be removed, and at — 80° nitric oxide, nitrous oxide and ammonia. Water and hydrazine, if present, were removed at 0°, and distilled into small tubes *in vacuo* and weighed. Gases were analysed by standard methods. In all experiments a satisfactory nitrogen, hydrogen and oxygen balance was obtained, the discrepancies never being larger than 2 per cent.

Liquid hydrazine was stored in a tube which could be connected to a glass bulb of about half a litre capacity. This bulb carried a mercury manometer, and was used for measuring the hydrazine before admission to the reaction vessel. The hydrazine was admitted to the bulb until a sufficient pressure was attained, and the whole was then distilled into the reaction vessel *in vacuo*.

In the study of the explosion of hydrazine, a cylindrical pyrex reaction vessel was used (length 10 cm., diameter 3 cm.). This had two tungsten electrodes, the tips of which were separated by about 1 mm. at approximately the centre of the vessel. The whole was surrounded by the furnace and maintained at a uniform temperature of 100° C. The rest of the apparatus was exactly the same as previously described. A small induction coil was used as the source of the spark. In order to examine the effect of vessel diameter on the lower explosion limit, a few experiments were performed in a vessel of diameter 15 mm.

Preparation of Materials.

Hydrazine was prepared by dehydrating pure 100 per cent. hydrazine hydrate with solid potash. The liquid was refluxed with potash several times and finally distilled. It boiled sharply at 113.0°C . The distillate was then fractionated *in vacuo* and the middle fraction preserved and used for the experiment described below.

The vapour above the liquid was pumped off before each experiment, in case there was any small amount of decomposition of the vapour in contact with tap grease. Nitric oxide was prepared by the interaction of nitrites and iodides in dilute sulphuric acid solution and pumped as described in the previous paper. It was stored in a glass bulb. Ammonia was obtained from a commercial cylinder. It was fractionated carefully *in vacuo*, and the pure gas was stored in a glass bulb. Nitrous oxide was prepared by heating ammonium nitrate to about 170°C . The gas was passed through a trap at -80° to remove water and some higher oxides of nitrogen and finally condensed in liquid air. It was then fractionated *in vacuo* and the middle fraction collected and stored in a glass bulb.

Results.

I. The Explosive Reaction.

The explosion of hydrazine exhibits the usual lower and upper pressure limits. The former is undoubtedly determined by a surface effect, the limit being lowered as the diameter of the reaction vessel is increased. Thus with reaction vessels of diameters 15 and 30 mm., the lower explosion limits were reached at hydrazine pressures of 50 and 35 mm. respectively.

As mentioned previously the main products formed during the explosion are ammonia, nitrogen and hydrogen. The relative amounts of these products are markedly affected by the presence of inert gas. The results of a series of experiments are shown in Figs. 1 and 2.

These show the variation of the ratio NH_3/H_2 with the pressure of inert gas added to the hydrazine before explosion. The inert gases used are nitrogen and ammonia respectively. It will be seen that the ratio NH_3/H_2 increases with the inert gas pressure. Further, ammonia is more effective than nitrogen in quenching the explosion, the upper total pressure limits being 147 and 185 mm. respectively. In all cases, when explosion occurred, decomposition was complete.

The main products obtained during the explosion of mixtures of hydrazine and nitric oxide are nitrogen, hydrogen and water. Ammonia is also formed but falls off rapidly with increasing amounts of nitric oxide, while minute traces of nitrous oxide may also be detected. The volumes of hydrogen and ammonia formed are shown in Fig. 3. It will be seen that

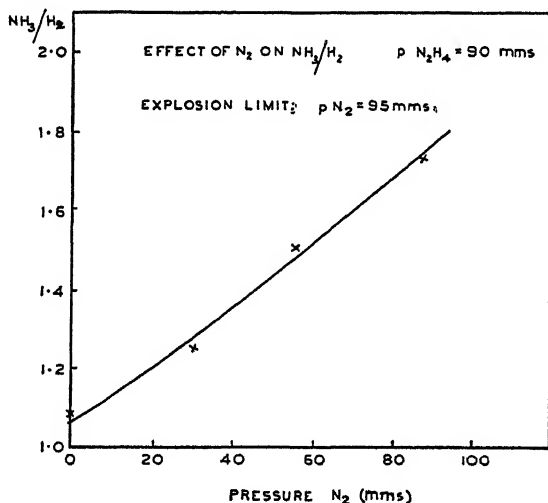


FIG. 1.

the volume of hydrogen exhibits a sharp maximum when about 30 mm. NO are present initially. Over the range in which the yield of hydrogen

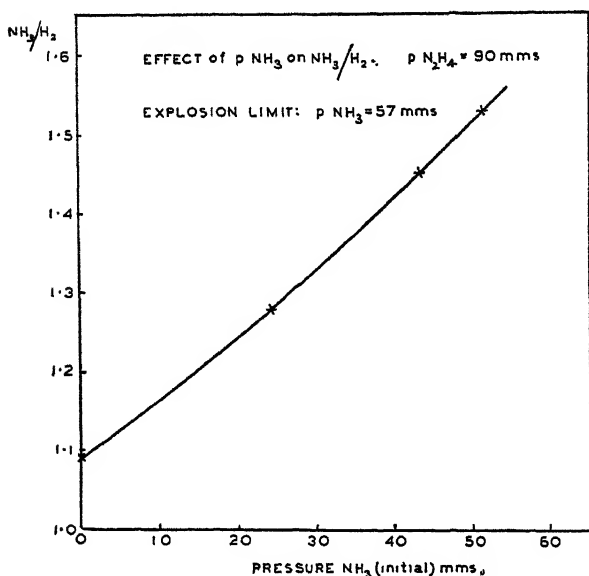


FIG. 2.

is increasing rapidly, formation of ammonia is decreasing rapidly, and for pressures of NO greater than about 30 mm. the amount of ammonia formed does not differ appreciably from 1.5 c.c. The maximum in the hydrogen curve corresponds closely to the part of the ammonia curve where the curvature is greatest. These facts suggested that there may have been some decomposition of ammonia into nitrogen and hydrogen in the heat of the flame and an experiment was tried to test this. A mixture of 90 mm. hydrazine, 75.5 mm. nitric oxide, and 50 mm. ammonia was sparked and the products analysed. The final volume of ammonia was

7.4 c.c., *i.e.* approximately that which would have been obtained in the absence of additional ammonia. On the other hand the yields of hydrogen and nitrogen were increased. The increase in the yield of hydrogen was 2.6 c.c. which corresponds to the decomposition of 90 per cent. of the

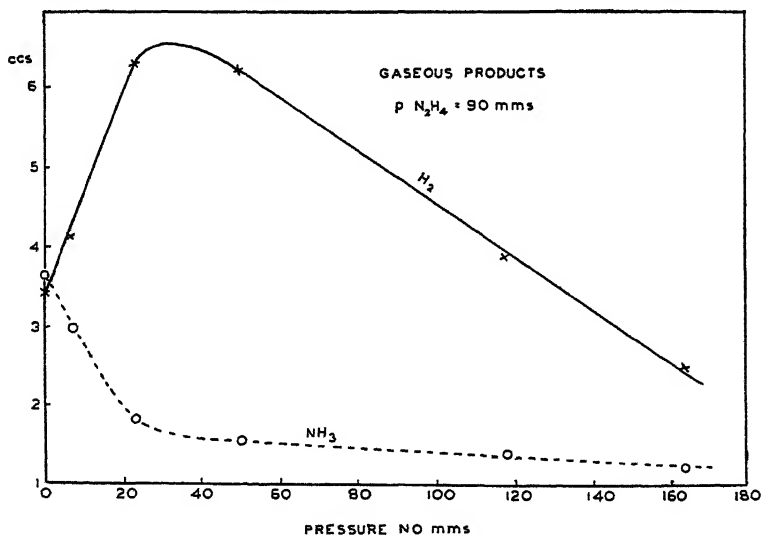


FIG. 3.

7.4 c.c., *i.e.* approximately that which would have been obtained in the absence of additional ammonia. On the other hand the yields of hydrogen and nitrogen were increased. The increase in the yield of hydrogen was 2.6 c.c. which corresponds to the decomposition of 90 per cent. of the

ammonia added initially (1.9 c.c.). In view of this result it is not unreasonable to suppose that the initial increase in the yield of hydrogen shown in Fig. 3 is due to the increasing thermal decomposition of ammonia as the pressure of NO is progressively increased (see p. 1245) and further it seems likely that the main products of the explosion of hydrazine vapour are ammonia and nitrogen, the thermal decomposition of some of the former being responsible for the hydrogen which appears in practice. This would account for the increase in the ratio NH_3/H_2 with added inert gas, the effect of the latter being to "cool down" the flame, and decrease the decomposition of ammonia. It will be noticed that the ratio NH_3/H_2 has a higher value at the explosion limit if nitrogen is the inert gas (1.8) than if ammonia is used (*ca.* 1.6). This is probably due to increased decomposition of ammonia in the latter case.

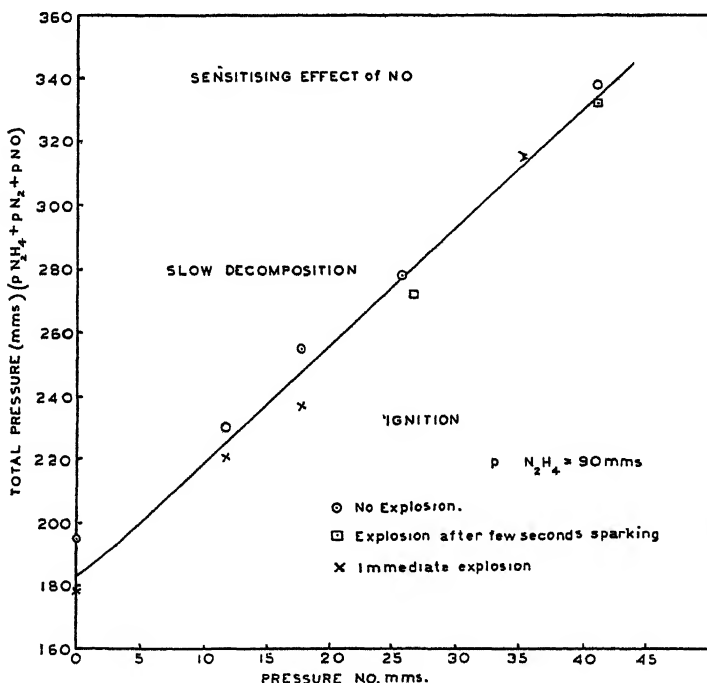


FIG. 4.

It was thought probable that N_2H_2 radicals participate in the explosion of hydrazine, and consequently that in the presence of nitric oxide, nitrous oxide would be formed.² Only traces (< 0.1 c.c.) could be detected however. This cannot be accepted as evidence against the participation of N_2H_2 radicals for it was shown that nitrous oxide added initially disappears during the explosion. In an experiment a mixture of 90 mm. hydrazine, 79 mm. nitric oxide and 41 mm. (1.5 c.c.) nitrous oxide was sparked. The remaining nitrous oxide measured less than 0.1 c.c.

The effect of nitric oxide on the upper explosion limit is marked. Addition of nitric oxide (at least up to 40 mm.) raises the limit, *i.e.* makes the mixture more explodable. This is shown in Fig. 4, in which the upper limit of explosion is plotted against the initial pressure of nitric oxide. A discussion of the bearing of these facts on the mechanism of the explosion is given later.

II. The Heterogeneous Decomposition in the Presence of Nitric Oxide.

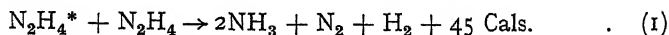
The details of some experiments are given below. The temperature was 310° C. in all cases.

No. of Expt.	Initial Pressures (mms.).		Products (c.c. at N.T.P.)			Ratios.	
	N ₂ H ₄ .	NO.	N ₂ .	NH ₃ .	N ₂ O.	N ₂ O/N ₂ .	NH ₃ /N ₂ .
1	56.6	30.8	3.6	5.3	1.1	0.31	1.47
2	30.2	29.2	2.5	4.0	1.1	0.44	1.60
3	30.7	50.5	2.4	3.0	0.9	0.37	1.25
4	30.5	100.0	2.5	2.7	0.7	0.28	1.08

The gaseous products are thus nitrogen, ammonia and nitrous oxide. It was easy to ascertain that water is also formed in the reaction. To facilitate the identification of this substance a decomposition was carried out until nearly all the hydrazine had decomposed. The water formed was then distilled out and identified by its physical properties, etc. It will be noticed that the ratios N₂O/N₂ and NH₃/N₂ decrease as the initial pressure of nitric oxide increases.

Discussion.

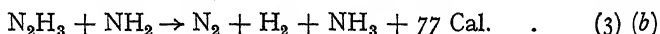
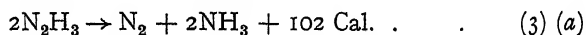
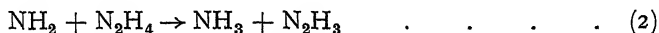
The elucidation of the mechanism of an explosion is always a matter of difficulty, and the following remarks should be regarded rather as tentative suggestions than an attempt to reach a final conclusion. Hydrazine is rendered more explodable by addition of nitric oxide (Fig. 4), the upper limit of explosion depending upon the pressure of nitric oxide in an approximately linear manner. This would seem to exclude any chain mechanism involving hydrogen atoms since the latter react rapidly with nitric oxide probably to form oximino radicals.¹ It is difficult to see how this reaction could be other than a chain stopping process, and the effect of nitric oxide in raising the upper limit cannot be explained by this mechanism. If we exclude the participation of hydrogen atoms it is not easy to construct a purely radical chain mechanism for the decomposition of hydrazine. The decomposition into ammonia and nitrogen is a strongly exothermic process, and it seems reasonable to suppose that the explosion is essentially thermal in nature. The simplest possible mechanism is that in which a hydrazine molecule is activated by the initial sparking and reacts with a second molecule thus :



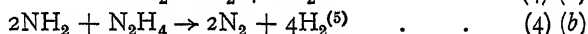
The heat of reaction is then handed on, wholly or partly, to fresh molecules of reactant, until, in the words of Norrish,³ one volume element, where there is the greatest intensity of reaction becomes adiabatic and self heating. This element then "fires off" the remainder of the gas. In practice more hydrogen is obtained than is predicted by (1), and as stated previously, this probably arises from thermal decomposition of ammonia. Alternatively we may suppose that instead of merely activating hydrazine molecules, the sparking actually ruptures them. Since the N—N bond is by far the weakest in the molecule, this would probably

³ Foord and Norrish, *Proc. Roy. Soc., A*, 1935, 152, 196.

be the one ruptured in the initial sparking process, or in collisions between hydrazine and other hot molecules. We may then write the following reactions :

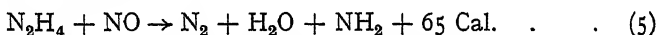


Reactions 3(a) and (b) have been previously suggested in other connections by Wiig and Kistiakowsky⁴ and by Mund and van Tiggelen⁵ respectively. On account of its highly exothermic character 3(a) would seem to be particularly efficient in propagating the explosion. Even if we assume the most unfavourable case, *i.e.*, that in which the heat of reaction of 3(a) is equally divided between the resultant molecules, each of the latter will (thermodynamically) have sufficient energy to dissociate a hydrazine molecule into 2NH₂. In addition to the hydrogen which arises from thermal decomposition of the ammonia, some may be formed by the reactions :

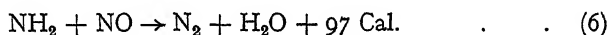


The upper pressure limit of explosion in the present case is probably to be ascribed to the deactivation of excited molecules by the inert gas present, while the lower limit is conditioned by a surface effect, *e.g.*, deactivation of hot molecules, adsorption of NH₂ radicals, etc.

In the case of explosion in the presence of nitric oxide, it is difficult to escape from the conclusion that NH₂ radicals participate in the reaction. The most probable reaction between excited hydrazine molecules and nitric oxide would appear to be :



The reaction closely resembles that which occurs between amino radicals and nitric oxide :



In the present case (5) would be followed by (6). If amino radicals participate in the explosion of hydrazine alone, then it is unnecessary to assume (5). The strongly exothermic nature of these reactions readily accounts for the effect of nitric oxide in raising the upper limit, and also for the rapid increase in the amount of thermal decomposition of ammonia, evidenced by the increased yield of hydrogen (Fig. 3) which occurs when the initial pressure of nitric oxide is progressively increased up to 30 mm. The decrease in the yield of hydrogen as the initial pressure of nitric oxide increases beyond 30 mm. is due to the increasing importance of (6) and/or (5), relative to the ammonia producing reactions (2) and (3).

The products of the heterogeneous decomposition in the presence of nitric oxide are easily explained by a similar series of reactions. If we assume the primary step is the effective dissociation of the adsorbed hydrazine molecule into 2NH₂, this would be followed by (2) and (3) probably occurring predominantly on the surface. The products in the absence of NO would then be ammonia and nitrogen in the ratio

⁴ Wiig and Kistiakowsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1806.

⁵ Mund and Van Tiggelen, *Bull. Soc. Chim. Belg.*, 1937, **46**, 104.

4 : 1 as observed by Askey² traces of hydrogen probably being formed by (4). In the presence of nitric oxide (6) begins to take place at the expense of (2), with the result that an increased yield of nitrogen is obtained. Further, reaction between N_2H_3 radicals and nitric oxide occurs¹



and accounts for the formation of nitrous oxide. The higher the pressure of nitric oxide the more will (6) predominate over (2), with the result that the yields of ammonia and nitrous oxide decrease relative to the yield of nitrogen, as observed experimentally (p. 1244). The primary dissociation of the hydrazine molecule into $N_2H_3 + H$ on the surface is less likely, since in this case increasing the pressure of nitric oxide should increase the ratio N_2O/N_2 while NH_3/N_2 would not be appreciably affected. The formation of nitrous oxide is evidence for the participation of N_2H_3 radicals in the decomposition.

When a vessel containing hydrazine vapour is heated non-uniformly an explosion occurs. This is probably brought about by NH_2 radicals formed by dissociation at the walls, leaving the latter and diffusing into a cooler region where the hydrazine concentration is still large enough to permit an explosion. In uniformly heated vessels the surface reaction is so rapid that by the time a temperature high enough to permit the escape of NH_2 radicals from the walls is reached, the bulk of the hydrazine has decomposed, and an explosion cannot occur.

Summary.

It has been found that hydrazine vapour explodes when sparked, the products being ammonia, nitrogen and hydrogen. The latter probably arises from the thermal decomposition of some ammonia. A brief study of the kinetics of the explosion has been made, and possible mechanisms are discussed.

The heterogeneous decomposition at a quartz surface in the presence of nitric oxide has also been studied, and as a result it is suggested that the primary step in the decomposition is the dissociation into $2NH_2$.

The author is indebted to Trinity College, Cambridge, for a Fellowship which made this work possible, and to the Chemical Society for a Grant for liquid air. He also wishes to express his thanks to Professor R. G. W. Norrish, F.R.S., for very helpful discussions.

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CALCULATIONS OF THE ADSORPTION BEHAVIOUR OF ARGON ON ALKALI HALIDE CRYSTALS.

BY WILLIAM J. C. ORR.

Received 13th July, 1939.

A number of authors ^{1, 2, 3, 4} have made calculations of the energy of interaction of a rare gas atom and an alkali halide crystal, which, from the theoretical point of view, is one of the best defined gas-solid adsorption systems. Lennard-Jones and Dent ² carried out calculations for the isosteric system Neon on NaF and Argon on KCl, making the assumption that the van der Waals and repulsive fields acting between an ion of the crystal and the rare gas atom were the same as those determined from an analysis of Virial coefficient data for two rare gas atoms. It was found that at the equilibrium distance above an ion the electrostatic field was about 10 % of the van der Waals' field, and that the position of lowest energy was actually above the centre of a lattice cell where the electrostatic field was zero. Lenel ⁴ has carried through accurate calculations of the van der Waals potential, using the London formula but evaluated the repulsive potential in a rather arbitrary way. It is now possible, however, to use explicit analytic expression for the repulsive potential and to calculate the total interaction energy and the equilibrium distance of an Argon atom adsorbed on any alkali halide surface without the use of any arbitrary constants. As regards experimental data to which these calculations may be applied, the only published heats of adsorption of the right order of magnitude are those of Lenel ⁴ for Argon on several alkali halides at rather low surface concentrations. The author ⁵ has, however, recently measured the adsorption of Argon and other non-polar gases on KCl and CsI and determined accurately the heats of adsorption from low concentrations up to the point at which bulk condensation of the adsorbed phase sets in. In the present paper are developed the calculations (necessary to interpret these results) of (1) the energy of interaction of Argon atoms with KCl and CsI surfaces, and (2) the energy changes that occur as a first layer is built up and as a second layer begins.

Calculation of the Energy of an Isolated Argon Atom on the Surface of an Alkali Halide Crystal.

The calculation of the energy of adsorption of an atom over any point above any cubic lattice may be divided into three sections, namely the calculation of, (A) the van der Waals' potential, (B) the electrostatic potential, and (C) the repulsive potential. These will be considered in turn.

¹ Blüh and Stark, *Z. Physik*, 1927, **43**, 575.

² Lennard-Jones and Dent, *Trans. Faraday Soc.*, 1928, **24**, 92 ; 1932, **28**, 333.

³ Herzfeld, *J.A.C.S.*, 1929, **51**, 2608.

⁴ Lenel, *Z. physik. Ch.B.*, 1933, **23**, 379.

⁵ To be published shortly.

A. The Van der Waals' Potential.

At the present time possibly the most useful single formula of general applicability for calculating the total van der Waals' energy is that known as the Kirkwood-Muller,⁶ in which the energy of a pair of atoms, ions or molecules is given by :

$$\phi_{v.d.w.} = \frac{\alpha_1 \alpha_2}{\alpha_1/\chi_1 + \alpha_2/\chi_2} \cdot \frac{6mc^2}{R^6} \quad (1)$$

where α_1, α_2 are the polarisabilities and χ_1, χ_2 the diamagnetic susceptibilities of the atoms; m is the mass of an electron and c the velocity of light. Although this expression is admittedly empirical, it reproduces to within $\approx 15\%$ the total van der Waals' energy between pairs of rare gas atoms as derived from an analysis of second Virial coefficient data by Lennard-Jones.⁷ Further, its practical utility in calculating adsorption heats in other systems has been shown by Barrer.⁸ For the present systems the required values of α for the crystal ions have been derived by Mayer,⁹ and of χ by Hoare and Brindley.¹⁰ The values of α for the the rare gases have been measured by Cuthbertson,¹¹ and of χ by Mann.¹²

Expressing the distance above the lattice plane of a crystal in terms of $\rho = r/a$ where r is the perpendicular distance from the centre of the atom to the plane, and a is the lattice constant of the crystal, it is evident, using formula (1), that the total van der Waals' potential can be written :—

$$\Phi_{v.d.w.} = \frac{6mc^2}{a^6} \left[\frac{\alpha_0 \alpha_+}{\alpha_0/\chi_0 + \alpha_+/\chi_+} S_+(\rho) + \frac{\alpha_0 \alpha_-}{\alpha_0/\chi_0 + \alpha_-/\chi_-} S_-(\rho) \right],$$

where the numbers S_+ and S_- are summations involving inverse sixth powers of ρ and whose values depend on the particular position of the adsorbed atom with respect to the lattice cell. The subscripts (0, + and -) distinguish quantities referring to the adsorbed atom or molecule, the positive ion and negative ion respectively.

In order to make the treatment as general as possible, the following summations were carried out :—

$\sum_1 v.d.w.$

$\sum_1 \rho$ is the sum of the inverse sixth powers of the distances of a point from all the lattice points of a complete cubic lattice (lattice constant $a = 1$), extending to infinity, where the point is distant ρ normal to the surface plane and situated immediately above the centre of a lattice cell.

$\sum_2 v.d.w.$

$\sum_2 \rho$ is a similar summation when the point is a distance ρ above the lattice plane and lies on the perpendicular bisector of the lattice edge.

$\sum_3 v.d.w.$

$\sum_3 \rho$ is the summation when the point is distant ρ perpendicularly above any lattice point.

⁶ Muller, *Proc. Roy. Soc., A*, 1936, **154**, 624.

⁷ Lennard-Jones, *Proc. Phys. Soc.*, 1931, **43**, 461; Fowler, *Statistical Mechanics*, 2nd Edit., Chap. 10.

⁸ Barrer, *Proc. Roy. Soc., A*, 1937, **161**, 476; 1938, **167**, 392.

⁹ Mayer, *J. Chem. Physics*, 1931, **1**, 270.

¹⁰ Hoare and Brindley, *Proc. Roy. Soc., A*, 1937, **159**, 395.

¹¹ Cuthbertson, *ibid.*, 1910, **84**, 13.

¹² Mann, *Z. Physik*, 1936, **98**, 548.

Thus,

$$\text{v. d. W.} \quad \sum_1 \rho = 4 \sum_{0,1,2}^l \sum_{1,2,3}^m \sum_{1,3,5}^n \left[\frac{1}{\{(\rho+l)^2 + \frac{n^2}{2}\}^3} + \frac{2}{\{(\rho+l)^2 + m(m+n) + \frac{n^2}{2}\}^3} \right],$$

$$\text{v. d. W.} \quad \sum_2 \rho = 2 \sum_{0,1,2}^l \sum_{0,\pm 1,\pm 2}^m \sum_{1,3,5}^n \left[\frac{1}{\{(\rho+l)^2 + m^2 + (\frac{n}{2})^2\}^3} \right],$$

$$\text{v. d. W.} \quad \sum_3 \rho = \sum_{0,1,2}^l \sum_{0,1,2}^m \sum_{1,2,3}^n \left[\frac{1}{(\rho+l)^6} + \frac{4}{\{(\rho+l)^2 + m^2 + n^2\}^3} \right].$$

Since no simple analytic method is available for evaluating these expressions, they were summed numerically over at least the nearest 250 points and the remaining contribution determined by integration.

The results obtained are given in Table I.

TABLE I.

$\rho \cdot$	0	0.5	0.625	1.0	1.5	2.0
$\sum_1 \rho$	34.174	10.3208	—	1.5643	0.3658	0.1276
$\sum_2 \rho$	132.140	17.869	—	1.6825	0.3685	0.1286
$\sum_3 \rho$	∞	66.910	18.958	1.8710	0.3700	0.1289

In order to use these summations at values of ρ intermediate between those above calculated, analytic expressions were calculated to fit these exactly. The most suitable type of expressions for \sum_1 and \sum_2 were found to be:

$$\sum_1 \rho = \exp. (3.5316 - 0.3600\rho - 5.7418\rho^2 + 3.8082\rho^3 - 0.7705\rho^4).$$

$$\sum_2 \rho = \exp. (4.8838 - 2.0436\rho - 6.0402\rho^2 + 4.7764\rho^3 - 1.0561\rho^4).$$

For \sum_3 however, the most suitable expression found was:—

$$\sum_3 \rho = \frac{\pi}{6\rho^3} \exp. \left[1.7785 \left(\frac{1}{\rho} \right) - 1.3109 \left(\frac{1}{\rho} \right)^2 + 1.0546 \left(\frac{1}{\rho} \right)^3 - 0.2487 \left(\frac{1}{\rho} \right)^4 \right],$$

where $\frac{\pi}{6\rho^3}$ is the asymptotic expression for \sum at large distances. This formula was constructed to fit the calculated values exactly at $\rho = 0, \frac{1}{2}, \frac{5}{8}, 1$ and 2, leaving the value at $\rho = 3/2$ to test its adequacy as an interpolation formula. The empirical formula gives $\sum_3 (3/2) = 0.369$,

which compares satisfactorily with the value calculated directly, namely, 0.370. With these expressions it is now possible to calculate the sums S_+ , S_- in terms of \sum_1 , \sum_2 , and \sum_3 for any symmetrical position above the 100 face of any of the three types of cubic crystal.

For the cases of interest here we have:—

Lattice Type.	Simple Cubic.	Body Centred Cubic.
Above the centre of a lattice square.	$S_+ = S_- = \frac{1}{2} \sum_1 \rho$	$S_+ = \sum_1 \rho$ $S_- = \sum_3 (\rho + \frac{1}{2})$
Above the mid-point of a lattice edge.	$S_+ = S_- = \frac{1}{2} \sum_2 \rho$	$S_+ = \sum_2 \rho$ $S_- = \sum_2 (\rho + \frac{1}{2})$
Above a positive ion in the lattice plane.	$S_+ = (\frac{1}{2})^6 \left[\sum_1 \frac{\rho}{2} + 2 \sum_2 \frac{\rho + 1}{2} + \sum_3 \frac{\rho^2}{2} \right]$ $S_- = (\frac{1}{2})^6 \left[\sum_1 \frac{\rho + 1}{2} + 2 \sum_2 \frac{\rho}{2} + \sum_3 \frac{\rho + 1}{2} \right]$	$S_+ = \sum_8 \rho$ $S_- = \sum_1 (\rho + \frac{1}{2})$

B. The Electrostatic Potential.

In the case of the simple cubic crystal the electrostatic field is zero along a line perpendicular to the centre of a lattice cell and also along lines perpendicular to the mid-point of a lattice edge. The values of the resultant field $rF(\rho)$ above an ion of the crystal have been accurately calculated by Lennard-Jones and Dent² and are here reproduced in Table II.

TABLE II.—SIMPLE CUBIC CRYSTAL.

Calculated from Lennard-Jones and Dent's data.

ρ	1.0	1.2	1.4	1.6	1.8	2.0
rF_3	0.0468	0.0192	0.0079	0.0032	0.0013	0.0005

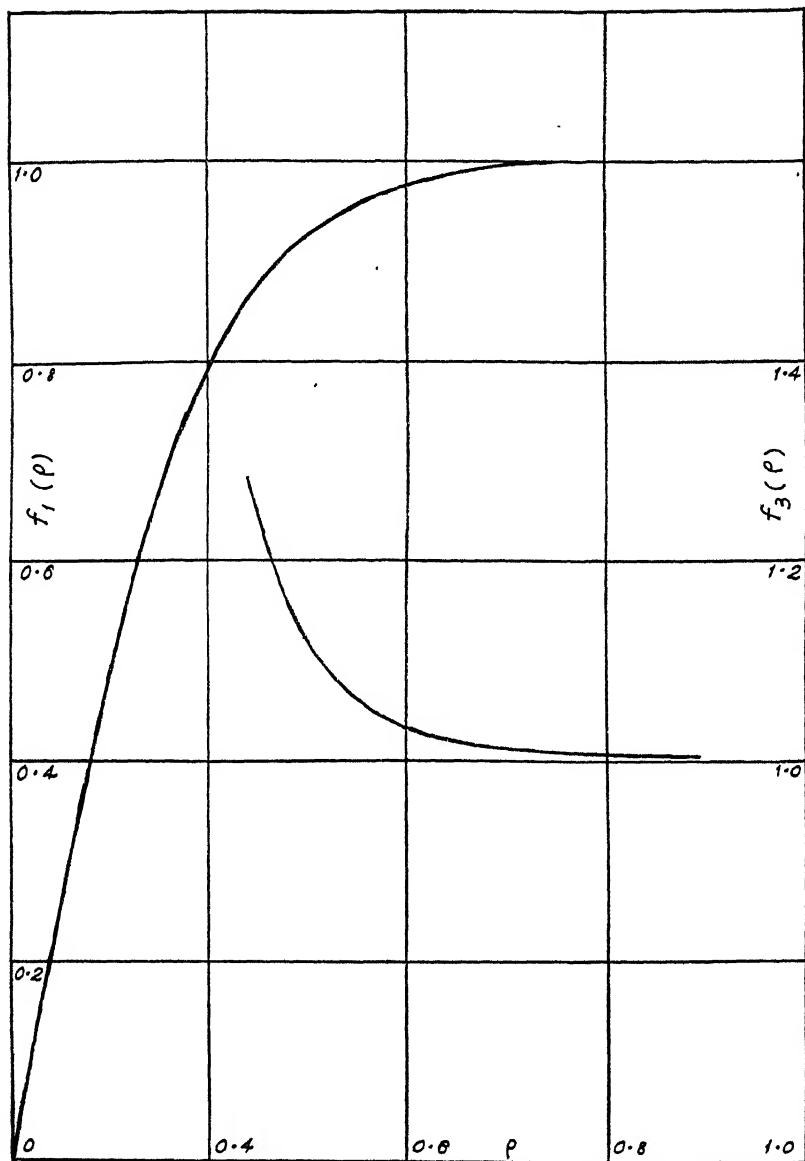
Since no calculations of the electrostatic potential above a body centred cubic lattice have been made, it was necessary to calculate these by direct summation.

The electrostatic fields f_1 and f_3 , normal above the centre of a lattice square and above a lattice point, due to a single layer of positive charges, may be defined as follows:—

$$f_1(\rho) = 4 \frac{e}{a^2} \sum_{1,2,3}^m \sum_{1,3,5}^n \left[\frac{\rho}{\left\{ \rho^2 + \frac{n^2}{2} \right\}^{\frac{3}{2}}} + \frac{2\rho}{\left\{ \rho^2 + m(m+n) + \frac{n^2}{2} \right\}^{\frac{3}{2}}} \right],$$

$$f_3(\rho) = \frac{e}{a^2} \sum_{0,1,2}^m \sum_{0,1,2}^n \left[\frac{1}{\rho^2} + \frac{4\rho}{\left\{ \rho^2 + m^2 + n^2 \right\}^{\frac{3}{2}}} \right],$$

f_1 and f_3 were evaluated by direct summation over 88.96 ions and the remaining contributions determined by integration. The values so obtained which are accurate to within 0.5 % are plotted in Fig. 1.

FIG. 1.—Electrostatic summations in units of $2\pi e/a^2$.

Now the total field due to a cubic lattice of positive ions will be :—

$$F^+(\rho) = \sum_{l=0}^{\infty} f(\rho + l),$$

and for a lattice of negative ions :

$$F^-(\rho) = - \sum_{l=0}^{\infty} f(\rho + l).$$

The resultant field rF in various positions will then be as tabulated below :—

Body Centred Cubic Lattice.	Surface Layer (+) Ions.	Surface Layer (−) Ions.
Above the centre of cell.	$rF_1^+(\rho) = F_1(\rho) - F_3(\rho + \frac{1}{2})$	$rF_1^-(\rho) = -F_1(\rho) + F_3(\rho + \frac{1}{2})$
Above a lattice point	$rF_3^+(\rho) = F_3(\rho) - F_1(\rho + \frac{1}{2})$	$rF_3^-(\rho) = -F_3(\rho) + F_1(\rho + \frac{1}{2})$

From Fig. 1, however, it is evident that within the present accuracy of calculation :—

$$rF_1(\rho) = f_1(\rho) - f_3(\rho + \frac{1}{2}) \dots \rho \geq 0.0$$

$$rF_3(\rho) = f_3(\rho) - f_1(\rho + \frac{1}{2}) \dots \rho \geq 0.5$$

The calculated values for these quantities as functions of ρ are given in Table III.

TABLE III.—BODY CENTRED CUBIC.

ρ .	0	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0
rF_1^+	-1.256	-0.580	-0.326	-0.230	-0.144	-0.072	-0.048	-0.027	-0.006
ρ	0.5	0.6	0.7	0.8	0.9	1.0	1.2	—	—
rF_3^+	0.259	0.118	0.064	0.032	0.019	0.011	0.005	—	—

The fields are in units of $\frac{2\pi e}{a^2}$.

A point of interest to note from these calculations is that the resultant field above the centre of a body centred cubic lattice cell is in the opposite direction to the field above an ion of the same surface. The resultant electrostatic energy in any given position of a non-polar molecule, whose polarisability is α , is then :—

$$\Phi_e = -\frac{1}{2}\alpha_r F^2.$$

(It should be noted that the summations shown in Fig. 1 and the calculations in Table III replace those given by Roberts and Orr,¹³ which were calculated over only the nearest 12 ions and are consequently less accurate.)

C. The Repulsive Potential.

An expotential expression, $\phi_R = cb_0 b_{\pm} \exp. (-r/0.345)$, (where $c = 10^{-12}$ ergs.) was used to calculate the repulsive forces between an adsorbed atom (o) and an ion of the crystal (\pm) for several reasons. Firstly, quantum mechanical calculations, in simple cases, indicate that the asymptotic expression for the repulsive potential may be expressed in terms of the form, $P(r)e^{-\beta r}$, where $P(r)$ is a polynomial in r , and β a constant. Born and Mayer¹⁴ found, however, that one term in which $\beta = 1/0.345$ and $P(r) = b_+ b_-$, where b_+ and b_- were parameters

¹³ Roberts and Orr, *Trans. Faraday Soc.*, 1938, **34**, 1346.

¹⁴ Born and Mayer, *Z. Physik*, 1932, **75**, 1.

characteristic of the ion involved was sufficient in calculations of the energies of the alkali halide and other cubic crystals. Secondly, Herzfeld¹⁵ found that, using a potential energy function in which $\phi_R = b_0^2 \exp. (-r(0.345))$ where $b_0^2 = 1340$, it was possible to calculate quite accurately both the Virial data and the heat of sublimation of Argon. It should be emphasised, however, that this form of repulsive potential with $P(r) = \text{constant}$, can be adequate only over a limited range of values of ϕ_R and must definitely be wrong for small values of ρ or large values of ϕ_R .

All the data required for calculating the repulsive energy between an Argon atom and any ion of an alkali halide crystal are thus accessible. The values of b_{\pm} required have been given by Huggins and Mayer.¹⁶

Now, as in case (A) and (B), the total repulsive potential has to be summed over all ions in the crystal. Thus it is necessary to evaluate summations such as the following example, which is for an atom above the centre of a lattice cell,

$$\sum_1^R (\rho, a) = 2 \sum_{0,1,2}^l \sum_{1,2,3}^m \sum_{1,3,5}^n \left\{ \exp. \left[- \left\{ (\rho + l)^2 + \frac{n^2}{2} \right\}^{\frac{1}{2}} / \frac{0.345}{a} \right] \right. \\ \left. - 2 \exp. \left[- \left\{ (\rho + l)^2 + m(m+n) + \frac{n^2}{2} \right\}^{\frac{1}{2}} / \frac{0.345}{a} \right] \right\}$$

when, $\Phi_R = b_0(b_+ + b_-) \sum_1^R (\rho, a).$

It is unfortunate that, with the repulsive potential in this form, these summations include a in the exponential term and so summations of general applicability for any lattice cannot be obtained. However, on the other hand, the convergence of these series is very rapid, as for example taking

$\rho = 1$ in the above series, $\sum_1^R (1.00, 3.14) = 2.8431 \times 10^{-5}$ when \sum' is the sum over 16 ions. Integration over the remaining ions to infinity gives an extra contribution of 0.00016×10^{-5} , which is entirely negligible. In all the present calculations Φ_R is calculated at each value of ρ by direct summation over the 14 to 16 nearest ions to the adsorbed atom.

The Total Potential Energy.

(1) KCl.—The total potential energy of an ion on the surface of a crystal is thus $\Phi = \Phi_{v.d.W.} + \Phi_e + \Phi_R$, the zero of energy being that of an atom at rest at an infinite distance from the crystal. The calculated potential energy-distance curves for an Argon atom situated over the centre of a KCl lattice cell, curve (1), above the mid-point of a lattice edge, curve (2), above a K^+ ion, curve (3⁺), and above a Cl^- ion, curve (3⁻), are shown in Fig. (2). From these curves the data collected in Table IV was calculated. The position of the minima gives directly the equilibrium distance r_e of the atom in any position above the surface. The depth of a trough at r_e is Φ_{\min} . By plotting the region round the minimum on a large scale, parabola $-\Phi = \frac{1}{2}f'(r - r_e)^2$ were fitted to all four curves giving the value of the restoring force per unit displacement, f' ,

¹⁵ Herzfeld, *Physic. Rev.*, 1937, 52, 374.

¹⁶ Huggins and Mayer, *J. Chem. Physics*, 1933, 1, 643.

of the atom normal to the surface in this region. The vibration frequencies were then calculated from the relation, $\nu_0 = \frac{1}{2\pi} \sqrt{f''/m}$ and the

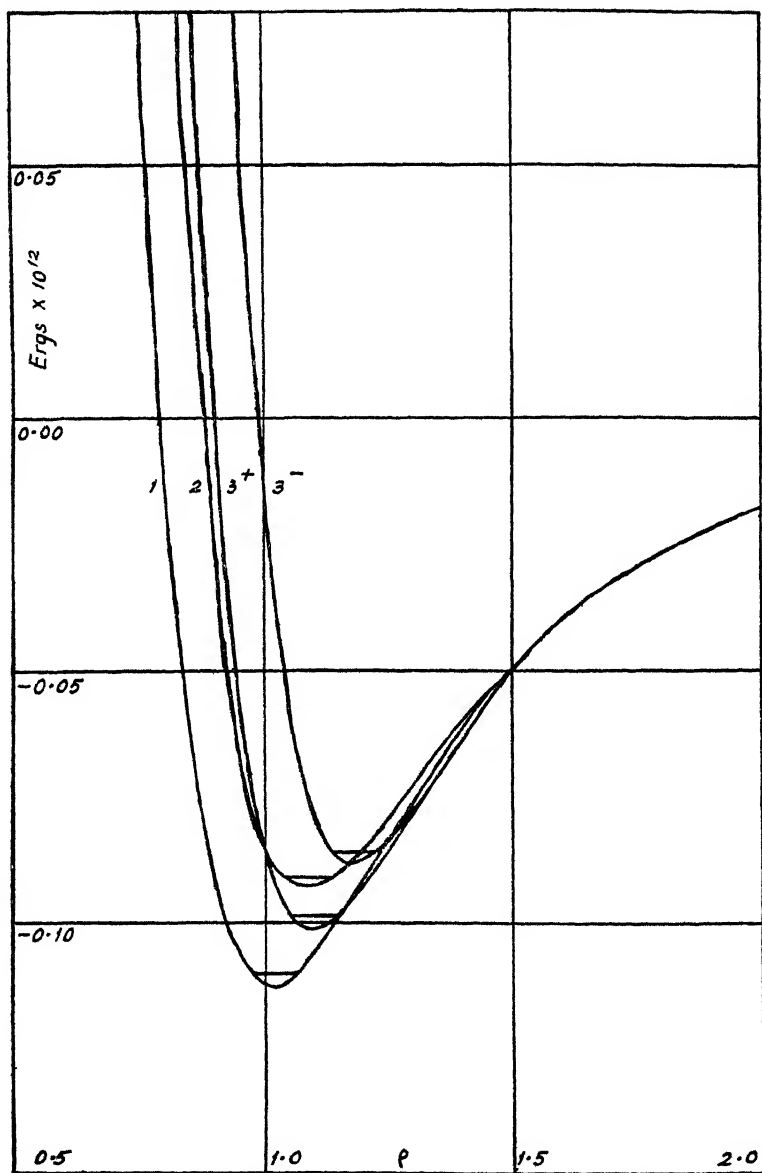


FIG. 2.—Argon on KCl.

zero-point energies from the relation, $\epsilon_0 = \frac{1}{2} h \nu_0$. Then the energy of the lowest vibrational state of the atom on the surface is $\Phi_{\min.} + \epsilon_0$. These values in cal. per gm. molecule are given in column 7.

TABLE IV.

	$r_e = a\rho_e$ (Å).	$r_{\text{eff. Argon}}$ (Å).	$-\phi_{\text{min.}} \times 10^{13}$ (erg./mol.).	ϕ_e/ϕ_p d W. (at ρ_e).	f' (dyne-cm. ⁻¹).	$\nu \times 10^{12}$ (sec. ⁻¹).	$\epsilon_0 \times 10^{18}$ (erg./mol.).	$-E_0$ (cals./g. mol.).
Above the centre of a lattice cell . . .	3.215	2.10	0.1132	0	2600	1.00	0.0033	1593
Above the mid-point of a lattice edge . .	3.44	2.02	0.0934	0	1710	0.81	0.0027	1314
Above a K ⁺ ion . . .	3.48	2.15	0.1015	4 %	2600	1.00	0.0033	1423
Above a Cl ⁻ ion . . .	3.74	1.93	0.0882	2 %	2260	0.93	0.0031	1233

From these figures an approximate potential energy surface for the system Argon—KCl may be constructed. In diagrams *a*, *b* and *c* of Fig. 4 cross-sections of the potential surface are drawn, the curves joining the calculated points being sketched in approximately. From these curves the plan of the potential surface, Fig. *d*, was constructed, the contours marking equipotential lines. The use of this diagram will be described in the following section.

(2) CsI.—The results calculated for Argon on CsI are shown in Fig. 3. The potential energy curves for the atom adsorbed above an ion are normal, but in the case of adsorption above the centre of a lattice cell, where the attractive fields are especially strong, the expression for the repulsive potential is quite inadequate, and leads to impossibly small equilibrium distances. However, if the value of b_0 in $\Phi_R(\rho)$ is adjusted to make the minimum of the potential curve fall at $\rho = 0.37$ (*i.e.* the value which would be expected from the sum of the effective radius of Argon determined from curves 1 and 2 and the ionic radius of Cs⁺), the potential curves behave normally. A minimum is obtained at this position when $b_0 = 1.3 \times 36.6$ instead of 36.6, giving curve (4) instead of curve (4*a*). Similarly, curve (3) is obtained in place of curve (3*a*), for the case of an atom above the centre of an I⁻ lattice square, when this value of b_0 is used. The values of $\Phi_{\text{min.}}$, r_e , ϵ_0 and E_0 obtained from curves 1, 2, 3 and 4 (Fig. 3) are collected in Table V.

TABLE V.

	Surface Layer.	$r_e = a\rho_e$ (Å).	$r_{\text{eff. Argon}}$ (Å).	$-\phi_{\text{min.}} \times 10^{12}$ (erg./mol.).	ϕ_e/ϕ_p d W. (at ρ_e).	$\epsilon_0 \times 10^{18}$ (erg./mol.).	$-E_0$ (cals./g. mol.).
Above the centre of a lattice cell.	Cs ⁺ ions	(1.73)	(1.89)	.2215	22 %	.0029	3168
	I ⁻ ions	2.60	1.95	.1880	3 %	.0030	2682
Above a lattice point.	Cs ⁺ ions	3.65	1.89	.0828	1 %	.0031	1100
	I ⁻ ions	4.08	1.89	.0967	0.4 %	.0028	1361

The values of the effective radius of the adsorbed Argon atom calculated in Tables IV. and V. are in reasonable agreement with values

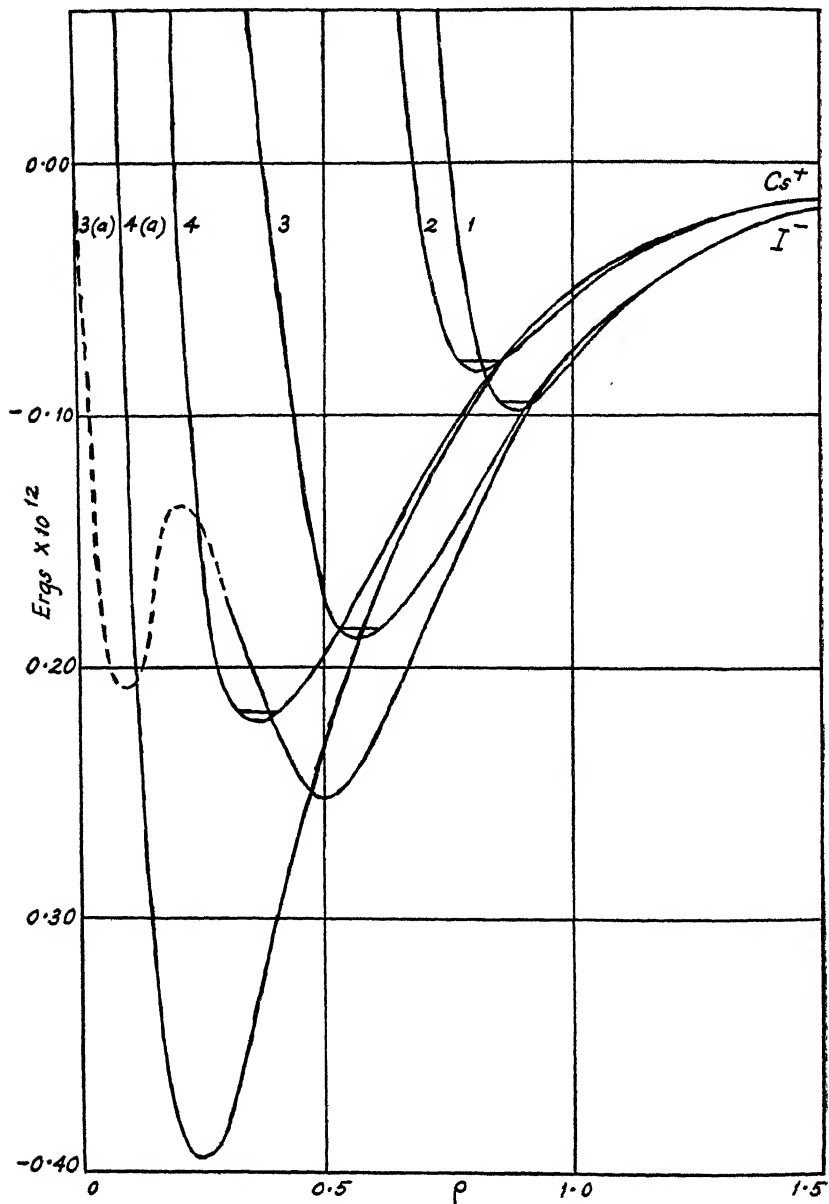


FIG. 3.—Argon on CsI.

determined otherwise; for example, X-ray measurements at liquid hydrogen temperatures¹⁷ give a value of 1.92 Å., while one obtains the

¹⁷ Simon and Simson, *Z. Physik*, 1924, 25, 160; Smedt and Keeson, *Leid. Comm.*, 1925, 178.

value 2.03 Å. from the density of liquid Argon¹⁸ at 87° K. The present calculations show how small in general the relative effect of the electrostatic potential is compared to the van der Waals. The case of an Argon atom adsorbed above the centre of a Cs⁺ lattice square is rather exceptional in that the atom can penetrate right into the surface layer and, in fact, makes contact with the layer of I⁻ ions lying below.

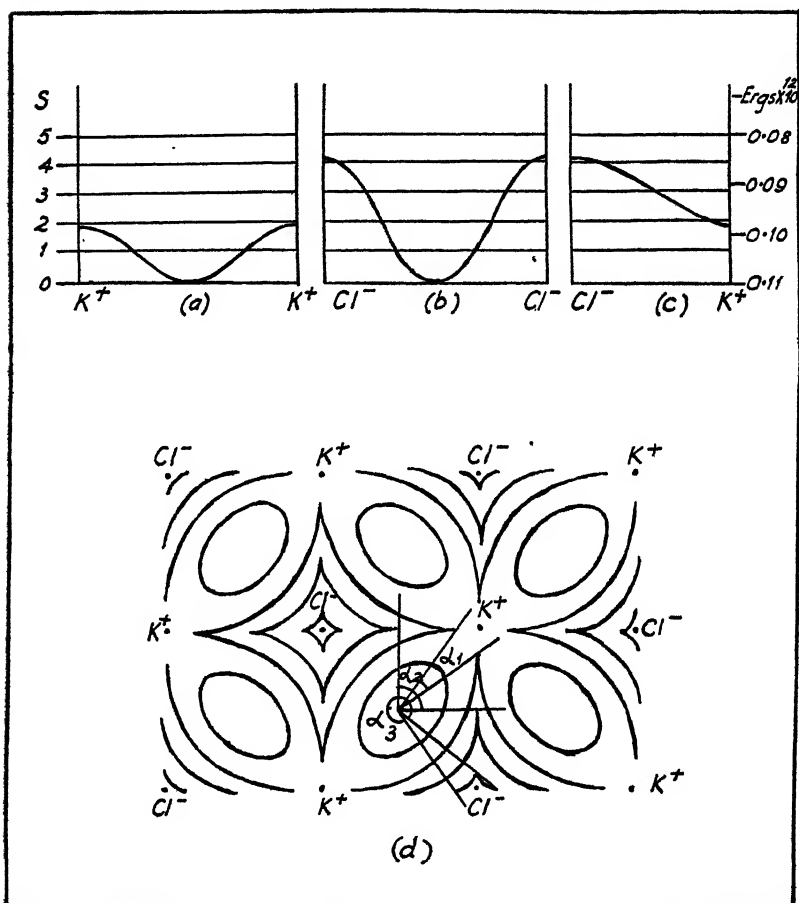


FIG. 4.

Section 1(b).

In a recent series of papers Lennard-Jones, Strachan and Devonshire¹⁹ have treated the quantum mechanical problem of an isolated rare gas atom vibrating normally with respect to a cubic lattice surface. Assuming that the potential energy of the system can be represented by Morse curve,

$$V = D[\exp. - 2\kappa(r - r_0) - 2 \exp. - \kappa(r - r_0)],$$

¹⁸ Baly and Donnan, *J. Chem. Soc.*, 1902, 81, 914.

¹⁹ Lennard-Jones and Strachan, *Proc. Roy. Soc., A*, 1935, 151, 442; Lennard-Jones and Devonshire, *ibid.*, 1936, 156, 6.

the discrete vibrational levels can be determined provided D and κ are known. From the previous calculations we have $D = -\Phi_{\min.}$ and, $\kappa = f'/2D$, so that for Argon situated above the centre of a KCl lattice cell we have $D = 0.1132 \times 10^{-12}$ ergs per molecule and $\kappa = 1.072 \times 10^8$ cm.

Using the following relations,

$$d = (2mD)^{1/2}/\kappa\hbar; \mu_s = d - s - \frac{1}{2} = (-2mE)^{1/2}/\kappa\hbar,$$

where $m = 39.91 \times 1.662 \times 10^{-24}$ g., $\hbar = 6.547 \times 10^{-27}/2\pi$ erg secs., we find that Argon may vibrate in a series of 35 discrete levels a few of which, are given in Table VI.

TABLE VI.

S	0	1	2	3	4	5	10	15	20	25	30	34
d	34.19	33.19	32.19	31.19	30.19	29.19	24.19	19.19	14.19	9.19	4.19	0.19
$-E_s$.1100	.1037	.0975	.0916	.0858	.0802	.0551	.0346	.0190	.0079	.0017	.0000
$N_s(80)$.4243	.2380	.1359	.0789	.0466	.0280	.0028	.0044	.0311	.043	.042	.042

The equipotential contours in Fig. 4d are drawn at the values of E_1 to E_8 given in the above table.

We may now make a calculation of the extent to which the heat of adsorption varies with the temperature.

Starting with the assumption which is definitely very approximate that the energy levels given in Table VI. for the case of an atom vibrating normally with respect to the surface are not significantly altered when the atom can move in a plane parallel to the surface, the thermal energy of the adsorbed phase, $\int_0^T [C_V]_{\text{ads.}} dT$, can be written thus:—

$$\int_0^T [C_V]_{\text{ads.}} dT = \int_0^T n [C_V]_{\text{ads.}} dT + \int_0^T p [C_V]_{\text{ads.}} dT,$$

where

$$\int_0^T n [C_V]_{\text{ads.}} dT = -[E(0) - \bar{E}(T)] \times 1.449 \times 10^{16} \text{ cal./g. mol.},$$

and

$$\bar{E}(T) = \sum_s N_s E_s, N_s = \exp. (-E_s/kT) / \sum_s \exp. (-E_s/kT).$$

To determine the thermal energy parallel to the surface, an estimate must be made of the relative number of atoms migrating and vibrating at any instant. Although a classical solution of this problem could possibly be obtained by first, writing out the probability that an atom in any element of volume δv would have sufficient kinetic energy to pass over the potential barrier in its line of motion and then, integrating this expression over all angles and over the whole volume of the potential basin, which would have to be defined by a suitable analytic function, this would be by no means a simple calculation to carry through. For the present purpose a rough estimate of the order of magnitude of this effect will suffice. We assume that the probability that an atom in a level

S will pass from one lattice cell to a neighbouring one, is given by $\sigma_s = \frac{\alpha_s}{\pi}$,

where α_S is the angle in a plane parallel to the surface at the energy level E_S , measured from the centre of the lattice cell and subtended by the contours of the potential surface. From Fig. 4 we obtain the following table of values of σ_S .

TABLE VII.

S	0	1	2	3	4	> 5
σ_S	0	0	0.11	0.46	0.89	1.00

Then, dividing the energy parallel to the surface into a part due to vibrating atoms, for which as a rough approximation we shall assume a specific heat equal to two-thirds of that of solid Argon (λ_T),²⁰ and a part due to migrating atoms for which we assume a specific of R cals., we have,

$$\int_0^T C_V [C_V]_{\text{ads.}} dT = \int_0^T \left\{ \sum_S N_S \left[\frac{2}{3} \lambda_T (1 - \sigma_S) + R \sigma_S \right] \right\} dT.$$

Finally, to the present order of accuracy, the difference between C_p and C_V for the adsorbed phase can be neglected, so that the variation of the heat of adsorption, as a function of the temperature, may be calculated as follows, giving the values in Table VIII.

$$\Delta H_T = \Delta H_0 + \int_0^T \{ [C_p]_{\text{gas}} - [C_p]_{\text{ads.}} \} dT,$$

where

$$\Delta H_0 = \Delta E_0 = -E_0,$$

and

$$\int_0^T [C_p]_{\text{gas}} dT = \frac{5}{2} RT, \quad \int_0^T [C_p]_{\text{ads.}} dT = \int_0^T [C_V]_{\text{ads.}} dT.$$

TABLE VIII.—ENERGIES IN CALS./GRM. MOL.

$T^\circ K$	0	10	20	40	60	80
ΔH_T	1594	1641	1669	1679	1663	1632

The importance of this result is that since the difference at liquid air temperatures, between ΔH_T and $-E_0$ is well within the experimental error, it is quite justified to compare the calculated energies directly with the experimental values of ΔH .

The Variation in the Heat of Adsorption as a First Monolayer is built up.

Section 2a.

Roberts²¹ has calculated, using Wang's²² treatment, the variation of the heat of sorption with θ , due to van der Waals' forces ($\Delta \Phi_{\text{v.d.W.}}(\theta)$), and has also derived the expression,

$$\Delta \phi_s(\theta) = \frac{1}{2} \alpha \cdot r F^2 / \left(1 + \frac{9}{\alpha^3} \alpha \theta \right), \quad . \quad . \quad . \quad (2)$$

²⁰ Clusius, *Z. physik. Ch. B.*, 1939, **31**, 467.

²¹ Roberts, *Trans. Faraday Soc.*, 1938, **34**, 1342.

²² Wang, *Proc. Camb. Phil. Soc.*, 1938, **34**, 577.

for the variation in the heat with θ due to the lateral interaction of the induced dipoles produced in the adsorbed molecules by the electrostatic field of the crystal \mathcal{F} . In order to apply these results to the cases of Argon on KCl and CsI surfaces, it is only necessary to take account of certain geometrical features.

(1) **KCl.**—In the case of KCl, atoms will be adsorbed initially above the centres of lattice squares. Now, taking the effective diameter of an Argon atom in the direction parallel to the plane of the crystal surface, as equal to 4.05 Å. (a value derived from the density of liquid Argon at 87° K.), it is evident that atoms cannot be accommodated on adjacent centres of lattice squares (lattice constant of KCl = 3.14 Å.), but may form a square array along diagonally adjacent sites

$$(\text{distance apart} = \sqrt{2} \times 3.14 = 4.44 \text{ Å.}).$$

The increase in energy of adsorption per molecule at $\theta = 1$ due to lateral van der Waals' interaction is,

$$\Delta \phi_{v.d.w.}^{\square}(1.00; a_S) = \frac{1}{2} \left[-S_6^{\square} \frac{\mu}{a_S^6} + S_{12}^{\square} \frac{\lambda}{a_S^{12}} \right] = \frac{1}{1} \Phi^{\square}(1.00; a_S), \quad (3)$$

(since $\Delta \phi_e^{\square} = 0$ in the case of KCl), where λ and μ are the constants of the force field for two Argon atoms, derived by Lennard-Jones,⁷ from an analysis of the Virial coefficients and $S_6^{\square} = 4.641$, $S_{12}^{\square} = 4.064$, result from the summations of inverse sixth and twelfth powers of distances occurring in square packing (in the case of two-dimensional hexagonal packing, the corresponding summations are $S_6^{\nabla} = 6.360$ and $S_{12}^{\nabla} = 6.010$). Thus the increase in energy per molecule of an atom in a square array with $a_S = 4.44$, above that of an isolated atom will be

$$-\Delta \phi_{v.d.w.}^{\square}(1.00; 4.44) = 372 \text{ cal.}$$

The variation of $\Delta \Phi_{v.d.w.}^{\square}(\theta; 4.44)$ with θ for such an arrangement is given

in Fig. 5, curve 1. This, however, does not represent the system of greatest possible energy at $\theta = 1$, because, assuming hexagonal close packing, we obtain $\phi_{v.d.w.}^{\nabla}(1.00; 4.05) = 715 \text{ cal.}$ This figure has to be corrected

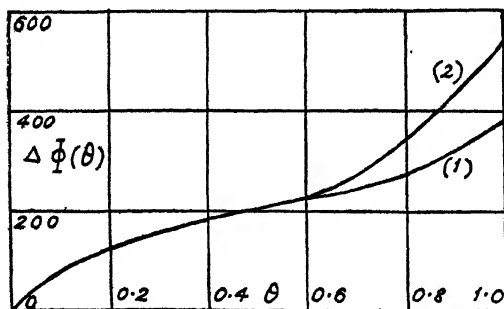


FIG. 5.

for the fact that the heat normal to the surface at $\theta = 1$ will be an average mean heat over all positions on the surface, whereas at $\theta = 0$ it is $-E_0 = 1593 \text{ cal.}$ Since the relative proportions of lattice centres, to the mid-points of lattice edges, to K^+ ions, to Cl^- ions is as, 2 : 2 : 1 : 1, the best mean value for the heat of adsorption of an atom, normal to the

surface in a hexagonally packed layer, is an average, weighted in this ratio, of the values in column 8, Table IV. The result is $-\frac{\Delta v}{KCl} E = 1412 \text{ cal.}$ This is a decrease of 181 cal. from the heat of sorption above the

centre of a lattice square, so that the total variation for this case at $\theta = 1$ is $-\Delta\Phi^\nabla(1.0) = 715 - 181 = 534$ cals., which is sufficiently in excess of the value for square packing to make the hexagonal arrangement much the more probable configuration.

The probable course of the theoretical $-\Delta\phi(\theta)$ variation will be that it follows curve 1, Fig. 5, closely from $\theta = 0$ to 0.5, but from $\theta = 0.5$ to 1.0 it will rise more steeply to reach the final value $-\Delta\phi^\nabla = 534$ cals., curve 2. In the above discussion the effect of the electrostatic field on $\Delta\phi^\nabla(\theta; 4.05)$ has been neglected, but this is justifiable, since it must certainly be smaller than $\Delta\phi_e^\square(\theta; 4.44)$ (which is the arrangement giving the maximum electrostatic effect for a simple cubic lattice), and which has the following values, 0, 9.2 and 16.4 cals. per gm. mol. at $\theta = 0, 0.5$, and 1.0 respectively.

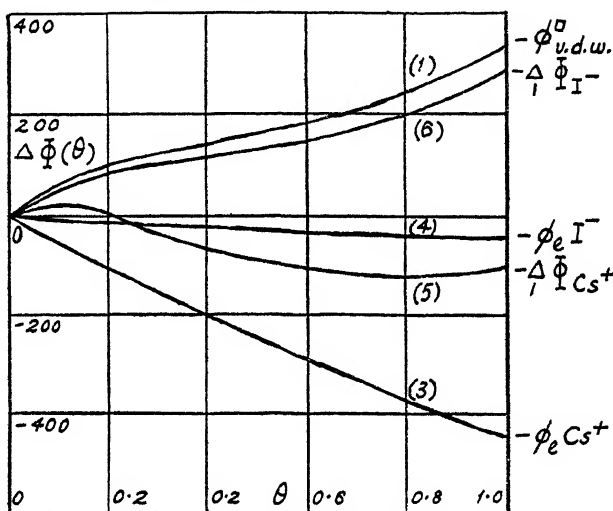


FIG. 6.

(2) CsI.—In the case of CsI crystals two distinct types of 100 faces, those consisting of Cs^+ ions and those of I^- ions, occur in equal proportions. At low values of θ , atoms will be adsorbed above the centres of lattice cells, and since the diameter of an Argon atom may be taken as 4.05 Å., which is smaller than the lattice constant of CsI, namely 4.56 Å., a square array of Argon atoms will be built up, one over each lattice cell. The extra van der Waals' energy per molecule at $\theta = 1$, due to this configuration is from formula (3),

$$-\Delta\phi_{v.d.w.}^\square(1.00; 4.56) = 327 \text{ cal. } \Delta\phi_{v.d.w.}^\square(\theta; 4.56),$$

plotted as a function of θ from Roberts calculation, is shown in curve 1, Fig. 6. The variation of the electrostatic energy $\Delta\phi_e(\theta)$ for Argon on Cs^+ and on I^- faces, calculated using formula (2), is shown in curves 3 and 4 respectively, Fig. 6. Curves 5 and 6 show the resultant heat variation, viz., $\Delta\Phi^\square(\theta) = \Delta\phi_{v.d.w.}^\square(\theta) + \Delta\phi_e^\square(\theta)$, from which it is evident that, in the case of atoms adsorbed on Cs^+ faces, the electrostatic repulsion due to the induced dipoles can be greater than the van der Waals'

lateral energy, while in the case of I^- faces, where the equilibrium distance of the atoms from the surface is considerably larger, being 2.60 Å. compared with 1.73 Å. in the previous case, the electrostatic field is very much weaker indeed. It is now necessary to show that for CsI, a square array of atoms represents a more stable system than a hexagonal array. The total energy of adsorption at $\theta = 1$, for square packing is, in the case of a Cs^+ face, $-E_0 - \Delta\Phi_{Cs^+} = (3168 - 120) = 3048$ cals., and for an

I^- face $= (2682 + 275) = 2957$ cal., using the values of $\Delta\Phi_{Cs^+}$ (1.0) and $\Delta\Phi_{I^-}$ (1.0) from Fig. 6. In the case of hexagonal packing, the adsorbed atoms will be distributed at random with respect to the lattice periodicities

and so $-\frac{\Delta\gamma}{Cs^+}$ and $-\frac{\Delta\gamma}{I^-}$ will be weighted averages of the values in column 7, Table IX, that is 2162 and 2022 cals., in the case of Cs^+ and I^- faces respectively. Moreover, since the electrostatic field changes sign between

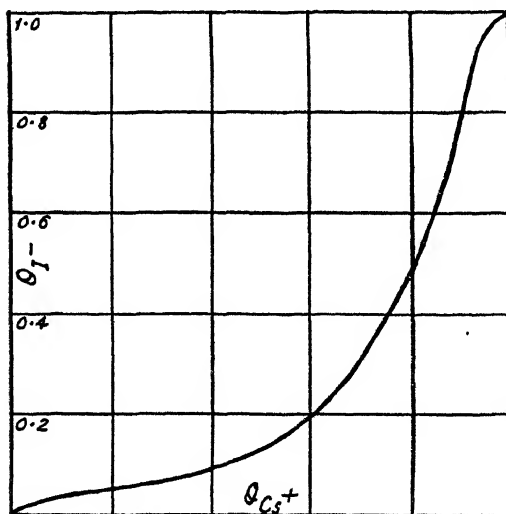


FIG. 7.

a position above the centre of a lattice cell and above a lattice point, $\Delta\phi_e^\gamma(\theta)$ may be put equal to zero, because it will have both attractive and repulsive terms, which tend on the average to cancel. Taking $-\Delta\phi_{e,d}^\gamma(1.00; 4.05) = 715$ cal., the total energy of adsorption of an atom in a hexagonally close packed layer will be $(2162 + 715) = 2877$ and $(2022 + 715) = 2737$ cal. respectively on Cs^+ and I^- surfaces. Since both these values are about 200 cal. less than the corresponding

values for square packing above lattice centres, we may presume that the latter is the more probable configuration.

We may now calculate the variation in heat of adsorption to be expected in the actual physical case where both Cs^+ and I^- faces are present and compete with each other for Argon atoms. At any equilibrium pressure p we have,

$$p = \frac{\theta_{Cs^+}}{1 - \theta_{Cs^+}} A_{Cs^+} e^{-\chi^+(\theta_{Cs^+})/kT} = \frac{\theta_{I^-}}{1 - \theta_{I^-}} A_{I^-} e^{-\chi^-(\theta_{I^-})/kT}, \quad (4)$$

where θ_{Cs^+} and θ_{I^-} are the fractions of the available surfaces of the Cs^+ and I^- faces covered with adsorbed atoms, $\chi^+(\theta_{Cs^+})$ and $\chi^-(\theta_{I^-})$ are equal to $-\frac{E_{Cs^+}}{1} - \frac{\Delta\Phi^\square}{1}(\theta_{Cs^+})$ and $-\frac{E_{I^-}}{1} - \frac{\Delta\Phi^\square}{1}(\theta_{I^-})$ respectively, and A_{Cs^+} can be put equal to A_{I^-} , since the partition function of an Argon adsorbed on a Cs^+ and on an I^- face will be almost exactly the same. Solving equation (4) graphically, the relation shown in Fig. 7 between θ_{Cs^+} and θ_{I^-} was obtained.

The average energy of adsorption of Argon on CsI crystals, as a function of θ , is then,

$$-E_{\text{CsI}}(\theta) = \frac{\theta_{\text{Cs}^+} \chi(\theta_{\text{Cs}^+}) + \theta_{\text{I}^-} \chi(\theta_{\text{I}^-})}{\theta_{\text{Cs}^+} + \theta_{\text{I}^-}},$$

where

$$\theta = \frac{1}{2}(\theta_{\text{Cs}^+} + \theta_{\text{I}^-}).$$

The course of $E_{\text{CsI}}(\theta)$ calculated in this way is shown in Fig. 8, curve 1, together with the curves for the variation in heat of adsorption with θ for the two faces separately.

Section 2b.

It remains now to discuss the behaviour of the adsorption system when the first layer is nearing completion and adsorption is beginning in the second layer. Dube²³ has already considered such a problem, assuming that the second layer atom can condense wherever four neighbouring atoms in the first layer condense to form a square. We shall now consider the equilibrium which results when it is assumed that the molecules, which condense in the second layer, behave as a 2-dimensional gas. This assumption must be very close to actual physical reality where the second layer is very dilute, which is just the case in which we are interested, where

$$0.8 < \theta, < 1.0.$$

If M_1 is the number of available positions for adsorbed molecules in the first layer and N_1 and N_2 the number of molecules adsorbed in the first and second layers respectively at equilibrium, then the total energies of adsorption for the first and second layers are,

$$N_1 \left(\chi_0 + \frac{1}{2} \frac{N_1}{M_1} \chi \right) \quad \text{and} \quad N_2 \delta_0,$$

where we assume that the configurational effects in the first layer can be represented by the Bragg and William's approximation, and that lateral interactions of the atoms in the second layer are negligible.

²³ Dube, *Proc. Cambr. Phil. Soc.*, 1938, 34, 587.

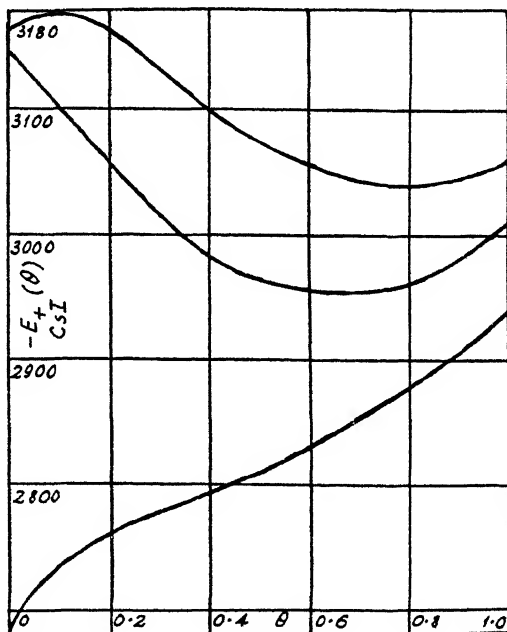


FIG. 8.

The Grand Partition Function for the whole adsorbed phase is then,

$$\Xi = \sum_{N_1=0}^{M_1} \frac{M_1!}{N_1!(M_1-N_1)!} \lambda^{N_1} e^{N_1(\chi_0 + \frac{1}{2} \frac{N_1}{M_1} \chi)} / kT \sum_{N_2=0}^{\infty} \frac{\lambda'^{N_2}}{N_2!} e^{N_2 \delta_0 / kT},$$

where,
$$\lambda = \lambda' = \frac{p}{kT} \cdot \frac{h^3}{(2\pi m kT)^{3/2} b_g(T)},$$

the various symbols having their usual significance in statistical formulæ.

This reduced to

$$\Xi = \sum_{N_1=0}^{M_1} \frac{M_1!}{N_1! (M_1 - N_1)!} (\lambda e^{\chi_0/kT})^{N_1} e^{\frac{1}{2} N_1 \frac{N_1}{M_1} \chi / kT} e^{\lambda' e^{\delta_0/kT}},$$

and since M_1 is large, we may equate $\log \Xi$ to \log (max. term.). Using Stirling's theorem and introducing $\theta_1 = N_1/M_1$, we have for the logarithm of the general term in the above summation,

$$M_1 \left\{ -\theta_1 \log \theta_1 - (1 - \theta_1) \log (1 - \theta_1) + \theta_1 \left(\log \lambda + \frac{\chi_0}{kT} \right) + \frac{1}{2} \frac{\theta_1^2 \chi}{kT} + \lambda' e^{\delta_0/kT} (=z) \right\}.$$

The maximum value of this expression (z) is obtained by substituting in it $\theta_1 = \theta_1^*$ where θ_1^* is the root of the equation,

$$\frac{\partial z}{\partial \theta_1} = -\log \theta_1 + \log (1 - \theta_1) + \log \lambda + \frac{\chi_0 + \theta_1 \chi}{kT} = 0.$$

Further, since,

$$\bar{N}_1 = \lambda \frac{\partial}{\partial \lambda} \log \Xi = \theta_1^* M_1,$$

and
$$\bar{N}_2 = \lambda' \frac{\partial}{\partial \lambda'} \log \Xi = M_1 \lambda_1 e^{\delta_0/kT},$$

we have
$$\frac{\bar{N}_2}{\bar{N}_1} = \frac{\lambda}{\theta_1^*} e^{\delta_0/kT},$$

that is
$$\frac{\bar{N}_2}{\bar{N}_1} = \frac{1}{1 - \theta_1^*} [\exp. (\delta_0 - \chi_0 - \theta_1 \chi) / kT] = \eta.$$

If we suppose that N_m = the total number of first layer sites, so that

$$\bar{N}_1 = N_m \theta_1,$$

we have
$$\bar{N}_1 + \bar{N}_2 = N_m (1 + \eta) = x.$$

Then, giving N_m , the arbitrary value 1.0, we can calculate the variation of the heat of sorption with the total number of molecules adsorbed (x), in the region round $\theta = 1.0$, since

$$-E(x) = \frac{\chi_0 + \theta_1 \chi + \eta \delta_0}{1 + \eta}.$$

For the case of Argon on KCl we may take $\chi_0 = -\frac{\Delta v}{E} = 1412$ cal. $\chi = \Delta \phi^\nabla (1.0) = 715$ cal. and $\delta_0 = 4 \times 240$ cal. where 240 cal. is energy

of a pair of Argon atoms at contact. η as a function of θ and $-E(x)$ as a function of x are plotted in Figs. 9 and 10. From Fig. 10 it is clear that the value of x_m at the maximum of the $-E(x)$ curve is within 1.0% of the value of N_m , the number of sites for adsorption in the first layer. Further, the energy at the maximum, namely 2080 cal., is depressed by only 47 cal. from the value that would be obtained at $\theta = 1$ namely,

$$\chi_0 + \chi = 2127 \text{ cal.}$$

if there were no competing adsorption in the second layer.

Summary.

Theoretical calculations are made for the adsorption systems Argon on KCl and on CsI of (1) the heats of adsorption and the equilibrium distances of the adsorbed atom at various positions on the surface, and (2) the variation of the heat of adsorption as a first layer of atoms built up and as a second layer begins.

I wish to express my thanks to Professor E. K.

Rideal, F.R.S., for encouragement and advice during the course of the work, and to Dr. J. K. Roberts and Dr. S. Levine for many helpful discussions. I am indebted to The Carnegie University Trust for the grant of a Research Fellowship, during the tenure which this work was carried out.

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Cambridge.*

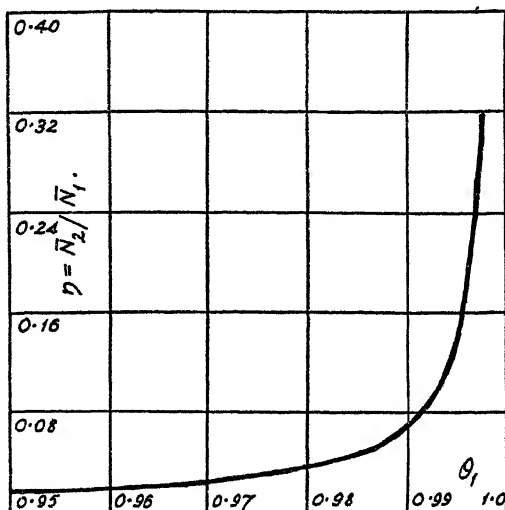


FIG. 9.

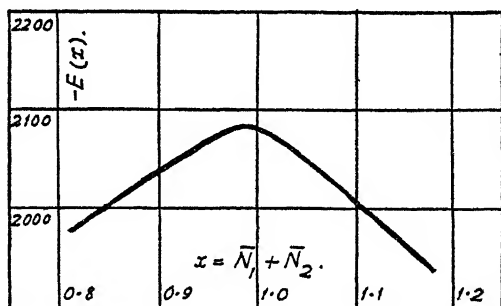


FIG. 10.

ON THE STRUCTURE OF PROTEIN FILMS.

By E. G. COCKBAIN AND J. H. SCHULMAN.

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It is known that many proteins when brought into contact with a water surface spread spontaneously to form thin films. The thickness of such films is much less than the diameter of the same proteins in bulk solution as determined by Svedberg, showing that the spreading process is accompanied by a change in the structure of the proteins. Examination of various protein films by measurement of the surface pressure and surface potential characteristics has been carried out by several investigators, but their results are only in qualitative agreement. In the present work, therefore, a further study has been made of wheat gliadin films, using the method of surface pressures and surface potentials. Information on the film structure has also been obtained by a study of the reaction between gliadin films and tannic acid present in the underlying solution.

Experimental.

The gliadin specimens employed were of a high degree of purity and, before use, were dried in air at 100° C. to constant weight. Buffer solutions usually consisted of $M/25$ KH_2PO_4 -NaOH mixtures made up according to the directions of Clark.¹ In experiments at pH 2.0, $N/100$ HCl substrates were used, measurements throughout being made at room temperature (17-22° C.).

Spreading of Proteins.

Gliadin films were prepared by spreading from 60 per cent. (by volume) aqueous ethyl alcohol solution of concentration less than 0.02 per cent. Mitchell² has shown that the area occupied by a gliadin film is independent of the concentration of the spreading solution when this is below 0.02 per cent. and agrees well with the area found by Hughes and Rideal³ who spread gliadin films directly from the solid. The question of complete spreading is a most important one in work on protein films. Before observations were made, therefore, an interval of two to five hours was allowed to elapse after spreading of the protein so that the film should attain a steady state. It was then found that the surface potential measurements became uniform at approximately the same area at which the film first exerted a measurable surface pressure (0.1 to 0.2 dynes/cm.). Thus it can be concluded that the films were in apparent equilibrium. The method of spreading employed by Gorter and Grendel⁴ consists in blowing a small quantity of an aqueous solution of the protein on to the water surface by means of a micropipette. These authors find that the rate of spreading is much greater at the iso-electric point of the protein than at pH values a little away from the iso-electric point, provided that the ionic strength of the substrate solution is low. We consider that,

¹ Clark, *The Determination of Hydrogen Ions*, Bailliere, Tindall and Cox.

² Mitchell, *Trans. Faraday Soc.*, 1937, **33**, 1129.

³ Hughes and Rideal, *Proc. Roy. Soc., A*, 1932, **137**, 62.

⁴ Gorter and Grendel, *Trans. Faraday Soc.*, 1926, **22**, 477.

when spread from aqueous solution, at least some of the protein is carried below the surface of the substrate and the rate of spreading is essentially the rate at which this protein reaches the surface, which will depend on the solubility of the protein in the underlying solution. The term "rate of spreading" in this connection is therefore rather a misnomer. We may note that if a very small amount of ethyl alcohol be added to an aqueous solution of a protein such as egg albumin, the protein spreads rapidly at all pH values.⁵ Philippi⁶ considers that the slow spreading of aqueous protein solutions on either side of the iso-electric point is due to the electric charge which they carry. Electric repulsion between molecules in the surface and in the solution means that work has to be done to bring the latter molecules into the surface. It is probable, however, that this is only one of the factors involved. The phenomenon is fundamentally the same as the changes in surface tension of protein solutions which occur over a period of several hours. The reason for these slow changes is still obscure. The surface tension of a protein solution, when a steady value has been reached, depends on the pH of the solution.⁷ Similarly, the area to which a protein film can extend when spread from aqueous solution varies with the pH of the substrate⁸ and the same factors are no doubt operative in both cases.

The fact that gliadin is readily soluble in 60 per cent. ethyl alcohol but insoluble in water or salt solutions makes it a particularly suitable protein to study.

Pressure-area and Surface Potential-area relations for Gliadin Films.

In Figs. 1 and 2 are shown the curves obtained at pH 2.0 (N/100 HCl) and 7.2 (M/25 phosphate buffer) by plotting the surface pressure F and the surface potential difference ΔV against surface concentration of gliadin (A) in metres²/mg. A is calculated on the assumption that all the gliadin spread remains on the surface. The F - A curves at the two pH values are very similar. At areas greater than about 1.6 m.²/mg., the pressure is not measurable on the surface balance used, i.e., F is less than 0.1 dynes/cm. In this region the surface potential is non-uniform, sometimes varying at different points of the surface by more than 100 mv. At pressures between 0.1 and 1.0 dynes/cm. approximately, the film is highly compressible, the area of the film in this region usually extending from about 1.5 to 1.0 m.²/mg. We find, however, that the area corresponding to the first measurable surface pressure (0.1 dynes/cm.) is not reproducible, often varying between 1.2 and 1.9 m.²/mg. In Figs. 1 and 2 the F - A curve at pressures below 1 dyne/cm. is therefore indicated by dotted lines which represent the average of a large number of experiments. The significance of the F - A variations at low pressures in relation to film structure is considered later. From a pressure of one to two dynes/cm. up to the collapse point, the film has a nearly constant compressibility, the actual value of which depends on experimental conditions. For example, the compressibility decreases as the time interval between complete spreading and compression of the film is increased, a behaviour which was also observed by Mitchell.² We do not find that the surface elasticity $-A dF/dA$ shows a maximum at about 10 dynes pressure, as was observed by Bateman and Chambers⁸ for egg-albumin films. With gliadin films, the surface elasticity is practically constant above pressures of 2 to 3 dynes/cm.

At both pH 2.0 and 7.2 the film is a liquid at high values of A , but on compression changes to a gelatinous state exhibiting elasticity and rigidity. On M/25 phosphate buffer at pH 7.2 the change liquid \rightarrow gel

⁵ D. G. Dervichian, *Private communication*.

⁶ Philippi, *On the Nature of Proteins*, Thesis, Amsterdam, 1936.

⁷ See Neurath and Bull, *Chem. Revs.*, 1938, **23**, 401.

⁸ Bateman and Chambers, *J. Chem. Physics*, 1939, **7**, 244.

is usually most marked at surface pressures of 9 to 13 dynes/cm., while on $N/100$ HCl the corresponding range is generally higher, 13 to 16 dynes/cm. In a few experiments on $N/100$ HCl, however, the film was definitely gelatinous at pressures below 2 dynes/cm. In these cases it was noticed that the first measurable surface pressure exerted by the film occurred at relatively low values of A , i.e. 1.1 to 1.2 m^2/mg . Surface potential measurements uniform to within a few millivolts were obtained at approximately the same surface concentration of gliadin as that at which the film showed a measurable surface pressure. The ΔV - A curves vary with the pH of the substrate. On $N/100$ HCl, ΔV rises on compression of the film to an approximately constant value of 420 mv., whilst at pH 7.2 the corresponding potential is 285 mv. However, when solid gliadin particles

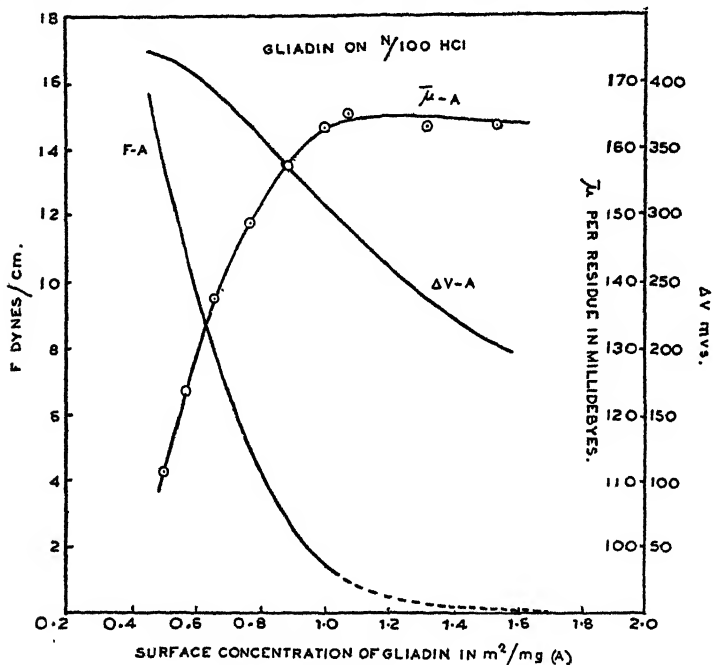


FIG. 1.

are spread on $M/25$ phosphate buffer at pH 7.2, ΔV reaches a constant value of 330 mv. at about 15 dynes/cm. pressure. The difference may be due to the retention of a certain amount of adsorbed ethyl alcohol when the gliadin is spread from aqueous ethyl alcohol.

The fundamental units from which proteins are built up are α -amino acid residues $-CHR-NH-CO-$ and the mean m . wt. of the residues in gliadin, as determined by chemical analysis, is 121. For a given surface concentration of gliadin the number of residues n , per cm^2 , can therefore be calculated and by substitution in the Helmholtz equation $\Delta V = 4\pi n \bar{\mu}$, the vertical component of the mean electric moment per gliadin residue ($\bar{\mu}$) is obtained. The variation of $\bar{\mu}$ with the surface concentration of gliadin, A , is shown in Figs. 1 and 2. At both pH 2.0 and 7.2, $\bar{\mu}$ is constant at areas greater than about 1.0 m^2/mg . but decreases rapidly at lower areas.

In a recent study⁹ on protein films, Langmuir has estimated the amount of protein in the surface monolayer by depositing the monolayer

⁹ Langmuir and Schaefer, *Chem. Revs.*, 1939, 24, 181.

on a barium stearate step-plate and measuring its optical thickness. The thickness of the dry deposited layer is taken to be equal to the thickness of the monolayer on the water surface, thus allowing a calculation to be made of the total amount of protein in the monolayer. In the case of wheat gliadin this was only 70 per cent. of the quantity applied to the surface. We do not consider that this is a reliable method of determining the amount of protein in a monolayer unless account is taken of the deposition ratio which in the case of gliadin might be considerably less than one. Dean, Gatty and Stenhagen¹⁰ have pointed out the fallacies involved in the assumption that the thickness of a protein layer deposited on a metal slide equals the thickness of the surface film on water.

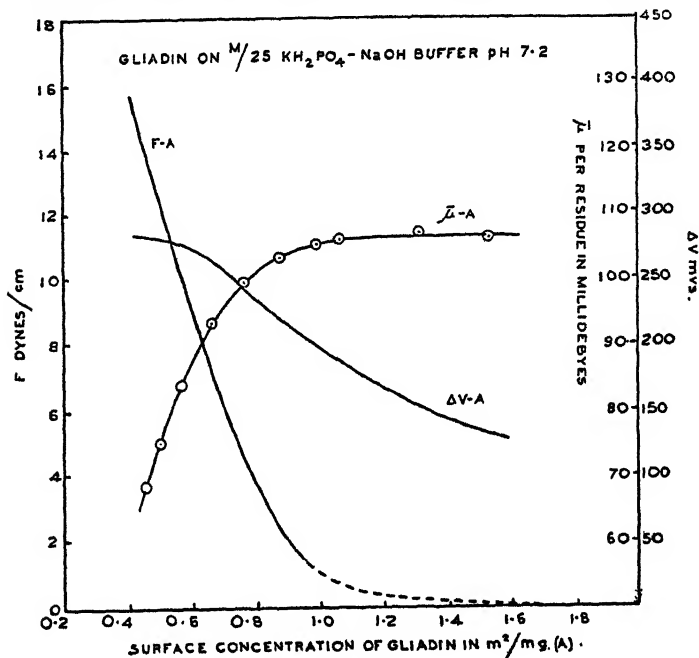


FIG. 2.

Interaction of Tannic Acid with Gliadin Films.

Schulman and Rideal¹¹ observed that injection of a small quantity of tannic acid solution underneath a gliadin film at pH 7.2 strongly affected the properties of the film. A rapid decrease in surface potential occurred and the physical state of the film changed from a liquid to a rigid solid. A gliadin film treated in this way could not be dispersed by injection underneath of potassium oleate solution. Schulman and Rideal concluded that the protein units in the film were strongly inter-linked by adsorption of the macromolecular tannic acid.

This reaction has been studied further in order to obtain data bearing on the structure of protein films. 20 mg. of dissolved tannic acid (resulting concentration in the substrate = 80 mg./litre) were injected under gliadin films at different initial surface pressures F_0 , the underlying solution being $M/25$ phosphate buffer of pH 7.2. It was found that the decrease in surface potential $\delta\Delta V$ of the gliadin film produced by the tannic acid

¹⁰ Dean, Gatty and Stenhagen, *Nature*, 1939, 143, 721.

¹¹ Schulman and Rideal, *Proc. Roy. Soc., B*, 1937, 122, 29.

was greater at low values of F_0 than at higher values. The effect is shown in Fig. 3, where the percentage decrease in potential $\frac{\delta\Delta V}{\Delta V} \times 100$ is plotted against F_0 . It appears that the basic side chains and peptide groups in the protein which react with tannic acid are not so readily available for

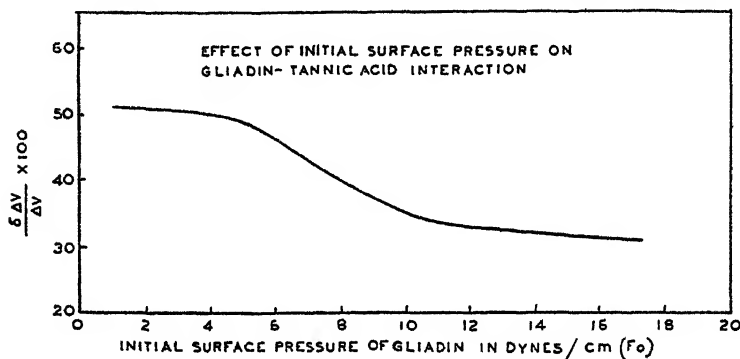


FIG. 3.

interaction when the surface pressure of the gliadin film is high. Injection of tannic acid solution under films of simple compounds such as stearic acid, cetyl alcohol, octadecylamine, stearamide, etc., has shown that at pH 7.2 tannic acid interacts strongly with films of amines, relatively weakly with amides and negligibly with acids and alcohols. Gliadin

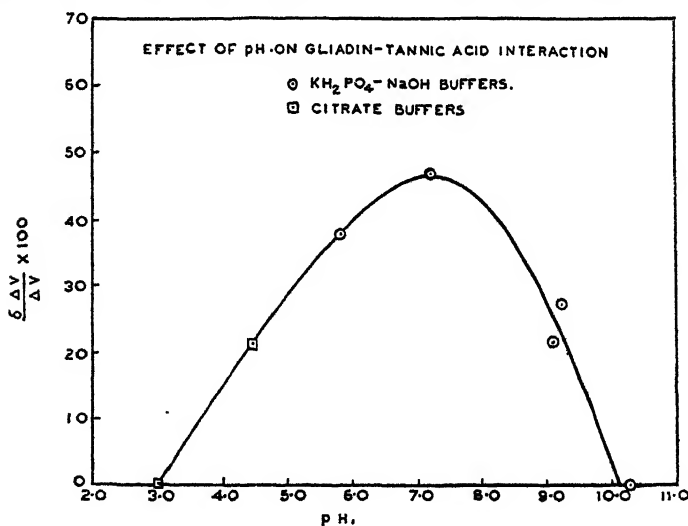


FIG. 4.

contains a much smaller percentage of the basic amino acids lysine, arginine and histidine than do most other proteins. It is probable, therefore, that as the surface pressure of a gliadin film is raised, both the basic side chains and the peptide chains themselves are less available for reaction with tannic acid. The percentage decrease in surface potential $\frac{\delta\Delta V}{\Delta V} \times 100$ produced by injection of 20 mg. of tannic acid under gli-

adin films at different pH values is shown in Fig. 4. The initial surface pressure of the films was 3.3 dynes/cm. in all cases. The maximum potential change occurs around pH 7.0 which indicates that the reaction is an ionic one involving negative tannate ions and positively charged centres in the protein. In connection with Fig. 4 it has been found that the potential changes depend markedly on the nature and concentration of the buffer salts present as well as on the actual pH of the buffer solution. Thus, with $N/1000$ NaOH solutions (pH 11.0) a potential change is obtained equal to that on phosphate buffers at pH 9.0, whilst with soda-borax buffers at pH 9.2 the potential change is zero.

Effect of Tannic Acid on Expanded Gliadin Films.

It has been shown previously¹² that if tannic acid be injected under a film of octadecylamine, at pH 8.0, expanded to large areas, then a coherent solid film exerting a pressure of about 1 dyne/cm. is obtained at areas greater than 60 \AA^2 per amine molecule. The film, being a rigid solid, collapses on compression. On phosphate buffer alone at pH 8.0 a film of octadecylamine occupies an area less than 30 \AA^2 /molecule.

Corresponding experiments have been carried out with expanded gliadin films on $M/25$ phosphate buffers at pH 7.2. The gliadin was spread at an area of 4.0 m^2 /mg. and left for two hours to reach apparent equilibrium, after which 20 mg. of tannic acid were injected into the underlying solution. The surface pressure remained too small to measure. On gradual compression of the film, the first observable rise in pressure (0.1 dynes/cm.) occurred at $A = 1.7 \text{ m}^2$ /mg. and at this point the film changed from a liquid to a rigid gelatinous state. Further slight compression caused the surface pressure to increase rapidly, but the film was clearly collapsing at pressures greater than about 0.5 dynes/cm. In a control experiment, in which no tannic acid was injected, an $F-A$ curve of the form shown in Fig. 2 was obtained, the first observable rise in pressure occurring at $A = 1.7 \text{ m}^2$ /mg., the same value as that obtained in the presence of tannic acid.

Discussion.

The effect of tannic acid on expanded gliadin films, in contrast to the effect on amine films, indicates that at large areas the spread gliadin is in the form of more or less compact micelles or islands with water spaces between. On injection of tannic acid, each micelle is converted into a gelatinous unit by adsorption of the acid, but the micelles are too far apart to be interlinked by tannic acid molecules. Hence, on compression of such a film the first measurable pressure will occur at the same area as that obtained for an untreated gliadin film. The tannic acid treated film, however, will appear gelatinous as soon as the "tanned" micelles are brought into contact, *i.e.*, immediately the rise in surface pressure commences. The $F-A$ and $\Delta V-A$ characteristics of gliadin films can also be satisfactorily explained on the view that the expanded films consist of micelles formed by the loose association of a number of protein molecules. At areas greater than 1.6 m^2 /mg. approximately the micelles are not in contact with one another and the surface pressure of any monomeric molecules in equilibrium with the micelles must be less than 0.1 dynes/cm. Big fluctuations of potential at different points on the surface are often observed in this region because the protein micelles are large enough to enable the movable electrode to pick out gross surface inhomogeneities. The micelles are first brought into contact at about

¹² Cockbain and Schulman, *Trans. Faraday Soc.*, 1939, **35**, 716.

$A = 1.6 \text{ m.}^2/\text{mg.}$ and we suggest that the $F-A$ region of high compressibility between $A = 1.6$ and $1.0 \text{ m.}^2/\text{mg.}$ corresponds to the elimination of water, partly from the inter-micellar spaces, but chiefly from the spaces between the molecules in the micelles themselves. Since no re-orientation of the molecules takes place in this process, the electric moment $\bar{\mu}$ remains constant (Figs. 1 and 2). As the protein molecules are assumed to be closely packed at $A = 1.0 \text{ m.}^2/\text{mg.}$, no further compression of the film can take place without a radical alteration in the structure of the film. The rapid decrease in $\bar{\mu}$ at areas less than $1.0 \text{ m.}^2/\text{mg.}$ and the decreased interaction of the film with tannic acid which occurs at surface pressures greater than about 4 dynes/cm. (Fig. 3) suggests that a re-orientation of the protein molecules takes place in the high pressure region such that the polypeptide chains and basic side chains are less available for reaction with tannic acid.

Stereochemistry of Protein Films.

According to the theory of Fischer and Hofmeister proteins consist of polypeptide chains built up from α -amino acid residues $-\text{CHR}-\text{NH}-\text{CO}-$. All the α -amino acids, except glycine, possess an asymmetric carbon atom and can exist in enantiomorphous forms. It is found that the α -amino acids obtained by degradation of proteins always possess the laevo configuration. The result is that when the polypeptide chain of a protein molecule is fully extended (β -keratin form) the side groups R project alternately above and below the plane of the $-\text{C}-\text{N}-\text{C}-$ backbone, as illustrated in Fig. 5a. In all the diagrams of Fig. 5 (unless stated otherwise) the plane of the polypeptide backbone is in the plane of the paper. Bonds in heavy type project above and bonds in dotted type project below the plane of the paper. From X-ray data it is known that the distance associated with the

repeating unit $\begin{array}{ccc} & \text{CO} & \\ & \diagdown \quad \diagup & \\ \text{CHR} & & \text{NH} \\ & \diagup \quad \diagdown & \\ & \text{CHR} & \end{array}$ in a fully extended polypeptide

chain is 3.5 Å, whilst the distance of closest approach of two such chains is about 4.5 Å. A monolayer of protein consisting of closely packed chains in the β -keratin configuration should therefore occupy an area per amino-acid residue (A_R) of 15.7 Å^2 , and attempts have been made to show that protein monolayers collapse when compressed to areas A_R less than 15.7 Å^2 . It is unlikely, however, that the polypeptide chains of a protein monolayer ever completely assume the β -keratin configuration. In the case of a protein such as gliadin, containing a large proportion of proline residues (approximately 13 per cent.), the β -keratin configuration is probably very unstable owing to the strain imposed on the proline rings. Molecular models show that this strain is greatly reduced if a bending of the main chain occurs at the points occupied by the proline residues, as shown in Fig. 5b. Further, the configuration of a polypeptide chain in a protein spread on water must be one in which all, or the great majority, of non-polar side chains are directed away from the water phase while all the polar side chains are directed into the water. This is borne out by the fact that on compression of a protein film, striations³ are ultimately formed which can be spun off the surface as threads. These threads are found to be hydrophobic and not respreadable on water. The β -keratin configuration does not fulfil these conditions even approximately in spite of the fact that many

proteins contain roughly the same number of polar and non-polar side chains. In gliadin, about 60 per cent. of the side chains are polar; if the distribution of side chains along the main chains were PNPNP PNPNP, etc., where P represents a polar and N a non-polar side chain, it can readily be seen that in the β -keratin configuration, half the polar side chains would be directed *away from* the water medium. Similarly, half of the non-polar side chains would be directed *towards* the water.

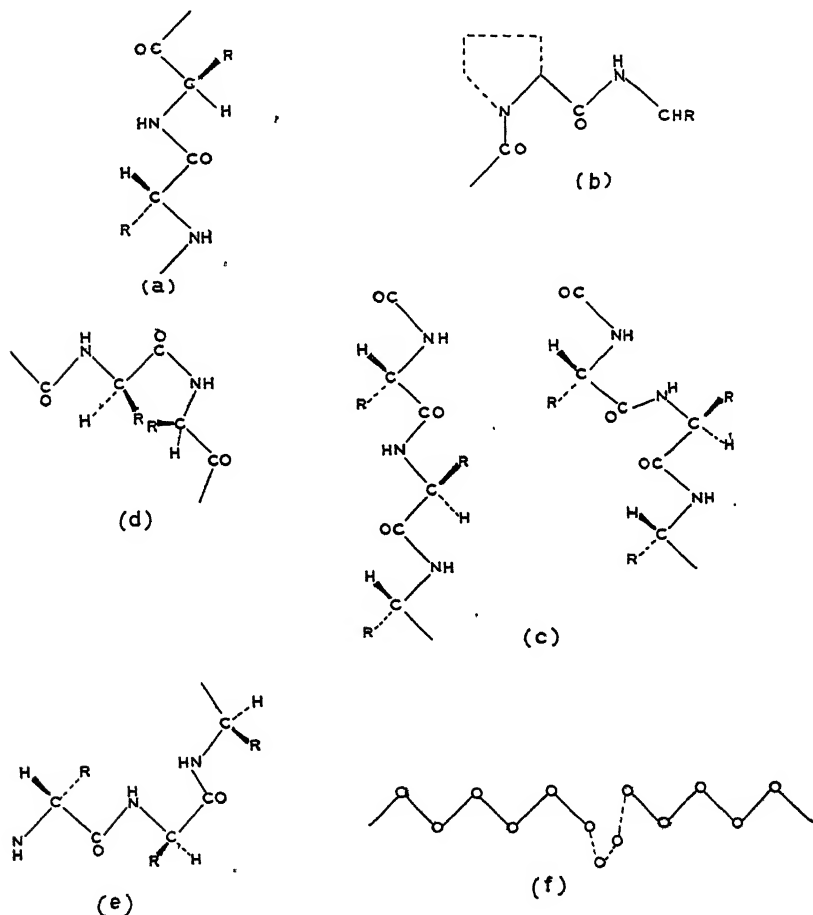


FIG. 5.

The possibility that free rotation round the single bonds of the side chains themselves occurs, when necessary, enabling the latter to leave or enter the water phase according to their non-polar or polar character, does not seem likely. Bent side chains would, of course, occupy a considerably greater area than straight chains, but the chief objection to this mechanism is that it does not remove from the water phase the short, non-polar side chains which are present in proteins. For example, a leucine residue when directed towards the water medium would remain almost completely immersed even when bent since the tetrahedral angle of the carbon valencies must be maintained. Thus, the

view that the polypeptide chains of a protein film possess a continuous β -keratin configuration is not probable.

However, bent configurations of the chain can be obtained by rotation round any of the single linkages constituting the backbone, and in this way the orientation of the side chains is also altered. If all the polar side chains are to be directed below, and all the non-polar ones above, the plane of the backbone, the latter must be bent to a certain extent. It need not be bent in a unique way since a number of configurations result in the same orientation of the side groups (see Fig. 5c). The possible configurations depend on the fraction of side chains which are polar and on the sequence of the polar and non-polar side chains along the main chain and therefore will be different for different proteins. Since hydrocarbon chains cannot be packed into an area much less than 20 \AA^2 , rotations of the polypeptide chain round the peptide links may be partially prevented when a protein is spread on water because not sufficient room is available for the side chains (Fig. 5d). However, rotation round the $\text{NH}-\text{CHR}$ or $\text{CO}-\text{CHR}$ linkages does not involve any steric hindrance effects (Fig. 5e). There is the further possibility of *partial* rotation round any of the single bonds of the polypeptide chain whereby the orientation of the side chains would be altered. In this case also, steric hindrance effects would be absent although the entire polypeptide chain would not be in one plane. (Fig. 5f.)

Thus we consider gliadin films, at surface pressures less than about 1.0 dynes/cm. , to consist of micelles in which the polypeptide chains are bent so that all, or nearly all, the polar side chains are directed towards, and the non-polar side chains away from, the water medium, while the polypeptide backbones themselves lie for the most part in a plane parallel to that of the water surface, but do not necessarily lie parallel to each other. At areas less than $1.0 \text{ m.}^2/\text{mg.}$ approximately (where the micelles reach a close packed condition) the polypeptide backbones are progressively turned from the plane of the water surface to an inclined plane. Owing to the bent configuration of the backbone the area per residue A_R can fall below 15.7 \AA^2 which is the minimum value possible for fully extended chains. In this way the existence of stable gliadin films at areas of $0.5 \text{ m.}^2/\text{mg.}$ ($A_R = 10.0 \text{ \AA}^2$) or even less can be accounted for. The re-orientation mechanism also accounts for the large decrease in electric moment $\bar{\mu}$ which occurs below $1.0 \text{ m.}^2/\text{mg.}$ and suggests an explanation for the decreased interaction with tannic acid at high surface pressures. The bends or loops in the polypeptide chains will project into the water phase (a loop above the water surface is likewise possible but involves a greater expenditure of work in its formation) and might prevent the peptide groups and basic side chains nearer the water surface from coming into contact with tannic acid molecules.

Gelation of Gliadin Films.

The change from the liquid to the gelatinous state which occurs on compression of a gliadin film is a gradual process, but is usually most noticeable at pressures between 8 and 16 dynes/cm. However, gelation sometimes occurred at pressures below 2 dynes/cm. and at areas as great as $1.0 \text{ m.}^2/\text{mg.}$ In these cases, the lowest measurable surface pressure (0.1 dynes/cm.) exerted by the film occurred at unusually low values of A , *i.e.* 1.2 to $1.1 \text{ m.}^2/\text{mg.}$, which indicates that in such films the protein micelles were more compact than usual. It is concluded therefore that

a suitable packing or adlineation of the polypeptide chains in the micelles aids the gelation process and that the variability of the gelation point is due to variations in the packing of the polypeptide chains. Several views have been put forward concerning the physical basis of gelation in protein films. Mitchell² has suggested the formation of co-ordinated hydrogen bonds between adjacent polypeptide chains. To obtain information on the interaction between carbonyl and imino groups present in compounds spread as monolayers, a study has been made on mixed films of stearomethylamide ($C_{17}H_{35}CONHCH_3$) and hexadecylurea ($C_{16}H_{33}NHCONH_2$). The physical properties of the mixed films were intermediate between those of the two components alone except that a deviation of the surface potential from the mean potential of the two components occurred. Similar results have been obtained with mixed films of stearomethylamide and acetoheptadecylamide. Thus the interaction between the carbonyl and imino groups seems confined to electrostatic dipole attraction since the formation of co-ordinated hydrogen bonds would be expected to result in a solid or gelatinous mixed film.

It is probable therefore that the forces causing gelation of protein films consist chiefly of simple dipole interactions between the polypeptide chains and between some of the polar side chains together with Van der Waals' forces of attraction between the hydrocarbon residues. As pointed out by Schulman,¹³ in the case of proteins containing an appreciable percentage of strongly basic and acidic side chains, the formation of salt-linkages will contribute to the gelation process, in the same way as the presence of long chain carboxylic acid molecules causes contraction and solidification of vaporous long chain amine films.

Summary.

The structure of protein films has been considered in the light of information revealed by a study of the force-area and surface potential-area characteristics of gliadin films and by the interaction of the films with tannic acid.

Stereochemical considerations are advanced in support of the view that separation of the polar from the non-polar side chains of a protein at an air/water interface takes place by means of a looping of the polypeptide chains. The mode of looping depends on the proportion of polar to non-polar side chains and on the sequence of these side chains along the main polypeptide chain. Reasons are given to show that protein films cannot consist of fully extended polypeptide chains of the β -keratin type or of any other regular polypeptide pattern as has usually been assumed.

At large areas gliadin films consist of two-dimensional micelles, as shown by the interaction with tannic acid. This is in marked contrast to the reaction between tannic acid and amine films.

On compression of gliadin films, water is first squeezed out of the intermicellar and intramicellar spaces, the apparent electric moment $\bar{\mu}$ remaining constant. Further compression, from about 2 dynes/cm. to the collapse point, results in a re-orientation of the protein units, the polypeptide chains being progressively turned from the plane of the water surface to an inclined plane. In this region the compressibility of the film is approximately constant. The gelation process is probably aided by a favourable adlineation of the looped polypeptide chains in the micelles. The forces causing gelation probably consist chiefly of simple dipole interactions, Van der Waals' forces of adhesion, and, in some cases, salt linkages.

¹³ Schulman, *Trans. Faraday Soc.*, 1937, **33**, 1122.

The interaction between gliadin films and tannic acid was shown to be strongly dependent on the pH , the nature and concentration of the anions in the underlying solution, and on the surface pressure of the film.

Our thanks are due to Professor E. K. Rideal for much help and stimulating discussion, to the Medical Research Council for a personal grant (J. H. S.) and to the I.C.I. Ltd. (Dyestuffs Group) for financial aid (E. G. C.) which made this work possible.

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REVIEWS OF BOOKS.

Die Theorie der Komplexität und der Allotropie. (153 diagrams.)

By Dr. A. SMITS (Amsterdam). Verlag Chemie, Berlin. R.M.
19.50.

Although Professor Smits' monograph was first published sixteen years ago, his ideas and experiments on the complex nature of some apparently unitary phases appear to be less well known than they deserve. Indeed the present volume contains several references to other workers who appear to be unaware of his pioneer work in this field.

Most students of physical chemistry find the concept of a component a difficult one to grasp until they are enlightened by studying a rigid deduction of the phase rule. The early chapters of Professor Smits' book deal in a simple way with the difficulties which arise in studying a particularly simple system containing two molecular species X and $(X)_n$. Should a system containing both types of molecules be regarded as a one or two component system? The author calls such an extra component $(X)_n$ which is not necessary to specify the stoichiometric composition of a phase a pseudo-component and the weakest part of his exposition lies in the absence of a clear formal definition of the meaning to be attached to this term.

Lack of such a definition leads him into some unguarded speculations which in the reviewer's opinion are quite inconsistent with a thermodynamic treatment of the subject. For example the identification of non-rotating states of the ammonium halides as pseudo-components would involve applying this term to a substance which, if it were separated as a pure phase, would not be in statistical equilibrium. Such a substance has no temperature or entropy in a thermodynamic sense, and thus cannot be a substance to which thermodynamic arguments can be applied. This objection, of course, does not apply to polymers or isomers which, if separated as a pure phase, would be as fit a subject for thermodynamic argument as any other unstable substance, *e.g.*, picric acid. This extension of the term pseudo-component is, however, quite unnecessary, and does not in any way affect the correctness of Dr. Smits' main argument.

The number of components required to describe a system containing both X and $(X)_n$ molecules appears first to have been considered by Gibbs (collected works, p. 141), and thermodynamic reasoning gives a

complete answer to the question. If the change $nX \rightleftharpoons (X)_n$ cannot occur then the system is a two-component system; if the change $nX \rightleftharpoons (X)_n$ represents a rapidly attained dynamic equilibrium the relationship between the phases observed will be that predicted by the phase rule for a unitary system.

For the intermediate state in which the transition $nX \rightleftharpoons (X)_n$ takes place at a rate to be measured on a human time scale, the phase relationships observed in the laboratory will depend upon other parameters than the thermodynamic variables of the system; it is now a matter of convenience whether the recorded measurements are expressed in terms of a thermodynamic nomenclature, which can no longer be strictly interpreted, since thermodynamic terms can only be applied to systems in equilibrium. Although the system in which the dynamic equilibrium $nX \rightleftharpoons (X)_n$ is rapidly maintained may be (and frequently is) described as a unitary system, it may be represented as a binary system in which the extra degree of freedom introduced by the extra component $(X)_n$ is suppressed by the extra condition which describes the equilibrium between the two components. The author is able to show, by reference to the phase diagrams of simple two-component systems, that the predicted phase relationships are those usually attributed to a unitary system exhibiting the phenomenon of allotropy. Whether any particular instances of allotropy are to be explained in this way is, of course, a matter which can only be settled by experiment and by far the most stimulating part of the monograph is the experimental section in which the evidence, that the allotropy of certain particular systems (notably phosphorus and sulphur trioxide) is in fact due to an inner internal equilibrium of the type described, is discussed. For the most part, this evidence consists in showing that the phase diagrams depend upon the time at which the observation is made, and change in a remarkable way when the components are carefully purified from substances which catalyse the rate at which the inner equilibrium is maintained. Other explanations may, of course, be found for any particular anomaly and whether the cumulative evidence is sufficient to enable one to agree with Professor Smits' conclusions is a matter for individual judgment. It is thus of particular importance that a start is being made in applying the new physical technique to these problems. Independent observations of the Raman spectra of sulphur trioxide show indications of molecular complexity, and it is to be hoped that further physical methods such as X-ray analysis and electron diffraction will soon be used to settle these important problems.

The book is well illustrated with phase diagrams and most of the argument is carried out in a simple straightforward way by reference to the diagrams, but analytical proofs of most of the theorems used are given in an appendix. It is well printed in Roman type, but the price is rather high by English standards.

Reports on Progress in Physics. Vol. V. (London: The Physical Society, 1939.) Pp. iv + 445. Price 20s.

The general scheme of this volume follows that of previous Reports. Advances in the normal branches of the subject (General Physics, Heat,

Sound, Atomic Theory, etc.) are dealt with in well-written and discriminating articles, to which are appended extensive lists of references. The book is, however, not merely a compilation of information on these branches; but contains also a dozen or more reports on specially selected subjects, and any assessment of its value will be influenced considerably by these special articles. The general impression gained is that they maintain a high standard in range, variety and treatment, the choice of those topics which shall be included having been made with considerable insight. The general reader will certainly find among these articles one or more which he will immediately desire to read and which he will not be able to find in a similar condensed form elsewhere. Where a subject is treated theoretically, the reports are not overburdened with mathematical work. Other articles are valuable because they give a good idea of the type of technical problem likely to be encountered in industry. Even the teaching of physics in schools claims some attention, albeit at the very end.

Of special interest to physical chemists are the articles on "Anomalies in applying Gibbs's adsorption theorem to dilute solutions exhibiting surface tension minima," "Theories of the Liquid State," "Plastics" and "The Soft X-Ray Spectroscopy of the Solid State," while the section on Spectroscopy contains a series of important articles. The reports on recent progress in Astronomy, Meteorology, Absolute Electrical Measurements and Electric Wave Filters are of more general interest.

There is brought together here in one volume what could only be gathered from a large number of scattered sources and an attractive survey is presented of those subjects in which students of physics should keep themselves up to date.

R. H. H.

The Alloys of Iron and Chromium. Vol. 1. Low Chromium Alloys.

By A. B. KINZEL and W. CRAFTS. (New York and London: McGraw-Hill Book Co., Inc. 1937. Pp. xv + 535. 36s. net.)

The commercial importance of chromium steels and the immense amount of investigation which has been carried out to determine their structure and properties has necessitated the volume of the "Alloys of Iron" series which deals with those of iron and chromium being divided into two parts. The first volume deals essentially with alloys containing up to ten per cent. of chromium, but the chapters devoted to these particular products are prefaced by five others (running to some 110 pages) in which attention is given to the constitution of the whole range of alloys. The first chapter, as is usual in this series of volumes, is introductory in character and contains a brief history of chromium steels, data re chromium minerals, the preparation and properties of chromium metal and of the commercially available forms of ferrochromium, the raw material used in the manufacture of chromium steels. In the next chapter the iron-chromium diagram is considered, and after reviewing published data the authors construct a probable diagram, which, except for the interpolation of dotted lines marking the possible range of composition in which the compound FeCr. may be formed by suitable annealing, follows closely that put forward by Adcock in 1931.

In the next chapter, the ternary Fe—Cr—C diagram is dealt with,

and the authors' summary of the present position is based very largely, as would be expected, on the recent and very exhaustive work of Tofaute and his colleagues. Might one suggest, however, that it is rather futile to include in a book of this description Krivobok and Grossmann's diagram for 22 per cent. chromium steels (published in 1930) as indicating the "nature of the section"? It was pointed out two or three years ago that the line drawn in this diagram to represent Ac.1 (and in others given by the same authors for higher contents of chromium) actually marks the minimum temperature from which retained austenite was obtained on quenching, and it bears hardly the slightest resemblance to the true Ac.1 line.

In summarising Tofaute's results, the authors appear to have slipped when they state "alloys containing 30 per cent. chromium contain only alpha, $(Cr.Fe)_4C$ and $(Cr.Fe)_7C_3$ phases. Hardening by heat treatment is therefore impossible." A reference to Tofaute's diagram shows that γ -iron is formed at suitable temperatures with 1 per cent. carbon and upwards. Actually 30 per cent. chromium alloys containing 2-3 per cent. carbon—such as are frequently used in the cast form for heat resisting purposes—harden quite intensely when rapidly cooled from temperatures of 900° or 1,000° C.

"Transformations in chromium steels" is the theme of the fourth chapter, and the voluminous data collected together by the authors serve to emphasize how much transformation temperatures in chromium steels depend on rates of heating and cooling (particularly the latter) as well as on other factors. Much of the data so laboriously obtained is true only under the specific conditions adopted by the particular investigators; values quoted for Ac.1, for example, and obtained on small samples heated at the ordinary rates frequently used for taking "thermal curves," may easily be 20 or 30 degrees above the temperature at which the steel would commence to transform when heated slowly.

In the next chapter the authors have attempted the difficult task of summarising the general effects of chromium on steel. Some of their generalisations seem to be rather wide and incidentally not too definite in meaning. For example, "as the chromium increases beyond 12 per cent., the strength and ductility in suitable carbon ranges continue to be improved, with the possibility of further improvement in wear resistance and creep strength" can hardly be regarded as typifying the views of those who have experience of the commonly produced alloys in this range of chromium contents. The qualifying phrase "in suitable carbon ranges" is probably its saving grace, through it might be as well to add that such "suitable carbon ranges" are not those generally employed. The authors appear to have realised that something else was required, because three lines further on they state "as the chromium passes 12 per cent. the possibilities of relatively soft material in the low carbon ranges appear and with constant low carbon content this ability to produce soft material suitable for deep stamping continues with increase of chromium up to 22 per cent." Unfortunately for this latter sentence, which suggests that relatively soft material sufficiently ductile for pressings is not obtainable below 12 per cent. chromium, the authors refer, a few lines further on, to a diagram giving the tensile properties of annealed steels containing 0.1 per cent. carbon and this shows that the tensile strength of such steels

increases slowly but practically regularly from 5 to 27 per cent. chromium, while the ductility, as represented by elongation, falls steadily over the same range of composition. The statement "even in plain chromium steels it is rare for any but minute percentages of austenite to be retained as such on rapid cooling," obviously requires modification.

On page 198, in describing the combined effects of carbon and chromium on response to heat treatment, the terms "hypo-eutectoid" and "hyper-eutectoid" have been reversed, and the description made still less clear by a reference to a diagram which appears to have little or nothing to do with the matter under discussion.

The remainder of the book consists of a detailed account, compiled from published data, of the properties of steels containing up to 10 per cent. chromium. Here the reader will find tables and diagrams galore, giving the results obtained by many investigators. The account is divided into a number of chapters, each dealing with some specified range of composition and each containing—in the manner customary in these volumes of the "Alloys of Iron" series—a summary by the authors of the useful properties of the particular group of steels.

In compiling this volume, the authors have obviously searched the literature very carefully so as to include all relevant matter. Undoubtedly some references have been missed and the reviewer noticed particularly one omission. In the Introduction, credit is given to Franks for the discovery of the effect of nitrogen on the properties of high chromium steels and reference made to patents which he apparently took out in 1935. Eight years prior to this, Adcock, at the National Physical Laboratory, had showed that nitrogen acted, in high chromium alloys, in a manner similar to carbon. The improvement in physical properties which Franks describes could be directly inferred from Adcock's account of the effects of nitrogen.

The second volume, which it is hoped will appear in the near future, will deal with the higher chromium alloys which are not only so widely used for resisting corrosion and heat, but are intensely interesting from a metallographical standpoint.

A Manual of Foundry Practice. By V. LAING and R. T. ROLFE, F.I.C.
2nd Edition, 1938. (Chapman & Hall, Ltd. Pp. viii + 312. 18s. net.)

This volume deals mainly with the founding and properties of cast iron. It also contains a chapter—which has been enlarged in the new edition—on non-ferrous castings. Limitations of space have prevented the authors extending the scope of the book to include sections dealing with the production of steel castings or such specialised parts of the industry as centrifugal or die casting.

The new edition contains about thirty-five pages of new matter, and within the field with which it deals, provides a good and essentially practical account of foundry practice, a result which might have been anticipated from the collaboration of the manager of a foundry and the chief metallurgist of a large engineering works.

ON THE SOLUBILITY OF GASES. PART I.—THE INERT GASES IN WATER.

BY D. D. ELEY.

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1. Introduction.

A fairly clear picture has been developed during recent years of the solubility of gases in *organic* solvents. To dissolve a gas molecule, a cavity has first to be made in the solvent, involving a positive internal energy change, $\Delta E_C/N$. The gas molecule is then placed into this cavity, $-\Delta E_A/N$ calories of energy being liberated. The internal energy change for solution of a mole of gas may then be written $\Delta E^0 = \Delta E_C + \Delta E_A$. If $-\Delta E_A > \Delta E_C$ the temperature coefficient of solubility will be negative and if $\Delta E_C > -\Delta E_A$ it will be positive. Kőrösy¹ has shown that in general this temperature coefficient is positive for gases with a critical temperature T_K under 180° K, and negative for those with T_K above 180° . Since the higher T_K the greater we might expect the solute-solvent interaction energy $-\Delta E_A$ to be, such a relation would arise for a series of gases in an organic solvent if ΔE_C is constant over the series in comparison with ΔE_A . Its application over a range of organic solvents indicates that the solvent molecules have similar force-fields. Uhlig² writes the free energy of cavity formation as $4\pi r^2\gamma$ where r = radius of cavity and γ = surface tension of solvent. He deduces an equation $kT \ln s = -4\pi r^2\gamma - \Delta E_A^*$, s being the Ostwald solubility coefficient. In this equation ΔE_A^* should really be written ΔG_A^* as strictly it is a Gibbs free energy, but this error does not affect his results. For a simple gas in a series of solvents Uhlig finds that $\ln s$ against γ gives an approximately straight line, from which he deduces a value of ΔE_A^* which is independent of the solvent used, depending only on the gas.

Water has anomalous properties as a solvent, and in this case, the regularities of Kőrösy and Uhlig break down. It is the purpose of this paper to show that in spite of this the simple picture already presented will account for the solution of the inert gases in water, and that it is possible to account theoretically, in an approximate manner, for the energies and entropies of solution that are observed over the temperature range 0° C. to 80° C.

The main features are that the exothermicity of solution of gases in water at room temperature is associated with the fact that ΔE_C is negligible. ΔE_C increases strongly over the range 0° to 80° C., however, and gives rise to a strong temperature dependence of ΔE , and so a

¹ Kőrösy, *Trans. Faraday Soc.*, 1937, **33**, 416.

² Uhlig, *J. Physical Chem.*, 1937, **41**, 1215.

curved plot for $\ln s$ against $1/T$. Our interpretation is that at low temperatures where the structure of water is important, solution can occur into positions between the quasi-lattice points. There is also the possibility of formation of low energy structures around the cavity. At higher temperatures water tends to pass into a close-packed liquid, and solution can only occur on to quasi-lattice points, involving a ΔE_0 comparable with the latent heat of evaporation of water.

2. The Solubility of the Inert Gases.

Lannung³ gives data on the solubility of He, Ne, A, (Kr, Xe, Rn), in water and six organic solvents. All these gases with one exception

show a positive temperature coefficient of solubility in organic solvents, and in all cases $\ln s$ against $1/T$ is a straight line. In these cases, $\Delta E_0 > -\Delta E_A$. The exception mentioned is Rn, the large polarisability of which may well make $-\Delta E_A > \Delta E_0$ and so lead to the negative temperature coefficient observed. On the other hand, in water the temperature coefficients of all these gases are negative and the $\ln s$ against $1/T$ plots are distinctly curved. Valentiner⁴ has also examined the solubility of the inert gases in water, and finds a negative temperature coefficient and a curved $\ln s$, $1/T$ plot. The results of Lannung and Valentiner do not agree in detail, but the exceptional behaviour of water is established. In Fig. 1 we present these data, together with that for N_2 , O_2 , CH_4 , H_2 and C_2H_6 for comparison. We will concern ourselves with the data of Valentiner⁴

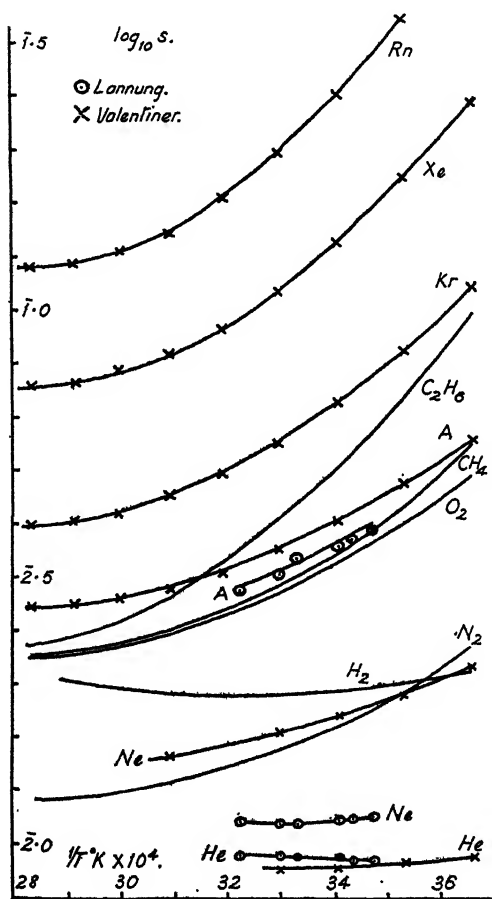


FIG. 1.

and proceed to evaluate ΔH^0 , ΔE^0 and ΔS^0 values in a form convenient for theoretical consideration.

³ Lannung, *J. Amer. Chem. Soc.*, 1930, **52**, 68.

⁴ Valentiner, *Z. Physik*, 1927, **42**, 253; *Landolt-Bornstein*, 5 Aufl., Erg IIa, 479.

We may write the free energy per mole of a perfect gas at a concentration of c_G moles per litre and temperature $T^\circ\text{K}$, as

$$\mu_G = \mu_G^0 + RT \ln c_G + RT \ln 0.082T.$$

Here μ_G^0 is the free energy of a mole of gas at 1 atmosphere pressure and is a function only of temperature. The partial molal free energy of a gas in dilute ideal solution is $\mu_S = \mu_S^0 + RT \ln c_S$ where c_S = concentration of gas in solution in moles per litre, and μ_S^0 = partial molal free energy of the gas in solution at a concentration of 1 mole per litre, and is a function of temperature and pressure only. At equilibrium $\mu_S - \mu_G = 0$, and we deduce

$$\mu_G^0 - \mu_S^0 = -\Delta\mu^0 = RT \ln s - RT \ln 0.082T. \quad (1)$$

We must note, that $\Delta\mu^0$ is the free energy change when a mole of gas is transferred from an infinite volume of gas at 1 atmos. pressure (concentration = 0.0446 moles per l.) to an infinite volume of solution at a concentration of one mole per litre. Valentiner has expressed his data for the inert gases by the formulæ

$$\log_{10} s = A/T + B \log_{10} T - X.$$

Inserting this value for $\log_{10} s$ in equation (1) we can then calculate $\Delta\mu^0$ and so ΔH^0 , ΔE^0 and ΔS^0 in terms of the values for A , B and X given by Valentiner.

$$-\Delta S^0 = \frac{\partial}{\partial T}(\Delta\mu^0) = R(-B - B \ln T + 2.3X + \ln 0.082T + 1) \quad (2a)$$

$$\Delta H^0 = -T^2 \frac{\partial}{\partial T} \left(\frac{\Delta\mu^0}{T} \right) = R(-2.3A + BT - T). \quad (2b)$$

$$\Delta E^0 = \Delta H^0 - p\Delta v = \Delta H^0 + RT. \quad (2c)$$

Valentiner's formulæ are for the range 0°C . to 80°C . and in Table I we present values of ΔH^0 and ΔS^0 calculated for four temperatures. We may remark that both ΔH^0 and $T\Delta S^0$ plotted against T give straight lines of slope $R(B-1)$. Lange and Watzel⁵ have similarly derived values of ΔH^0 and ΔS^0 , and observed their strong dependence on temperature. Deriving ΔE^0 by a method involving the latent heat of evaporation of water (giving values of 10 to 20 k.cal. mole⁻¹), they obtain values of $-\Delta E_A$ of 20 k.cal. or more for the larger inert gases. They rightly point out that these are too large to arise from Van der Waal's forces, and postulate some form of chemical bond between the inert gas and the water. We believe that a simpler alternative explanation of the behaviour can be given. Anticipating later calculations, we may remark

TABLE I.

Gas.	273.	293.	323.	353.
(A.) - ΔH^0 at $T^\circ\text{K}$, in k.cal. mole ⁻¹				
He	0.98	0.87	0.71	0.55
Ne	2.49	1.99	1.28	0.58
A	3.73	2.97	1.84	0.71
Kr	5.07	4.00	2.35	0.74
Xe	5.98	4.66	2.68	0.72
Rn	7.07	5.50	3.10	0.72
(B.) - ΔS^0 at $T^\circ\text{K}$, cal. deg ⁻¹ mole ⁻¹ .				
He	19.00	18.6	18.1	17.6
Ne	22.9	21.2	18.8	16.8
A	25.7	22.6	19.2	15.6
Kr	29.9	25.3	19.8	15.3
Xe	31.0	26.1	20.0	14.2
Rn	33.9	27.7	20.2	13.2

⁵ Lange and Watzel, *Z. physikal Chem. A*, 1938, 182, 1.

that the anomaly lies in the calculation of ΔE_{C} , which for the inert gas at 0° C. we consider to be negligible.

3. The Calculation of ΔE^0 and ΔS^0 .

We write, as previously, at temperature T

$$\Delta E_{\text{T}}^0 = \Delta E_{\text{C}, \text{T}} + \Delta E_{\text{A}, \text{T}} \quad (3a)$$

In a similar way

$$\Delta S_{\text{T}}^0 = \bar{S}_{\text{S}, \text{T}}^0 - S_{\text{G}, \text{T}}^0 = \Delta S_{\text{C}, \text{T}} + \bar{S}_{\text{A}, \text{T}}^0 - S_{\text{G}, \text{T}}^0 \quad (3b)$$

Here $\Delta S_{\text{C}, \text{T}}$ is the entropy change associated with the formation of a mole of cavities, $\bar{S}_{\text{A}, \text{T}}^0$ is the entropy per mole of the gas molecules in these cavities, and $S_{\text{G}, \text{T}}^0$ is the entropy of a mole of gas in the gas phase. In the calculations of ΔE^0 from a model we have to remember that*

$$\Delta E_{\text{A}, \text{T}} = \Delta E_{\text{A}, 0} + kT^2 \frac{\partial}{\partial T} \ln \frac{f_{\text{S}}}{f_{\text{G}}} \quad (4a)$$

$$\Delta E_{\text{C}, \text{T}} = \Delta E_{\text{C}, 0} + kT^2 \frac{\partial}{\partial T} \ln \frac{f'_{\text{W}}}{f_{\text{W}}} \quad (4b)$$

give the relation between the ΔE change at a temperature T and that calculated from a model at the absolute zero. Since we calculate ΔE_{C} from thermodynamical considerations equation (4b) is implicitly taken into account. (Here f'_{W} denotes the partition function for the water molecules in the solution, f_{W} for pure water.) If we consider water at 273° K. to be predominantly "crystalline," then later considerations indicate that we may write approximately $\Delta E_{\text{A}, 273} = \Delta E_{\text{A}, 0}$ (in equation (4a) f_{S} is the partition function of the gas molecule in solution, f_{G} in the gas phase). As will be seen, this is equivalent to the assumption that there is no change in structure between water at 273° K. and a hypothetical water at 0° K. Over the range 0° to 80° C. the second term in (4a) might become appreciable because of a change of structure of water with temperature. In (4b) however, the second term assumes a predominant importance, as included in the thermodynamic formula, for the variation of ΔE^0 with temperature.

4. The Calculation of ΔE_{C} and ΔS_{C} .

When a mole of gas dissolves in an infinite volume of solution at concentration of one mole per litre, a dilation of V c.c. occurs. We may write for a solvent $(\partial S / \partial V)_{\text{T}} = \alpha / \beta$ where α = thermal expansion coefficient and β = the compressibility (both considered as positive quantities). This formula holds for a small change in volume (where α and β are significant), and if we assume that α , β are the same for the solution as for the solvent, we may write the entropy change, which is essentially the entropy change associated with the formation of a mole of cavities to accommodate the gas molecules as

$$\begin{aligned} \Delta S_{\text{C}} &= \int_{V_1}^{V_2} \frac{\alpha}{\beta} dV = \frac{\alpha}{\beta} \cdot V. \quad (5a) \\ &= 0.0241 \frac{\alpha}{\beta} \cdot V, \quad \text{cal. mole}^{-1} \text{ degree}^{-1}. \end{aligned}$$

* See p. 1289.

The energy change is derived from

$$\left(\frac{\partial E}{\partial V}\right)_T = p + T\left(\frac{\partial S}{\partial V}\right)_T.$$

Since p is negligible we may write

$$\Delta E_C = T \frac{\alpha}{\beta} \cdot V = 0.0241 T \frac{\alpha}{\beta} V, \text{ cal. mole}^{-1} \quad (5b)$$

The numerical evaluation is for α in deg.^{-1} β in atmospheres⁻¹. In Fig. 2 we plot values of ΔE_C , calculated from this formula for $V = 10$ c.c., against T . (α calculated from *Smithsonian Physical Tables*, 1933, p. 168. β from *Landolt-Bornstein*, 5 Aufl. Hw.I., p. 100). We see that at room temperature ΔE_C (and also ΔS_C) is negligible, but that it increases strongly with temperature.* That it is just the ΔE_C , ΔS_C terms which give rise to the strong temperature dependence of the observed ΔE^0 , ΔS^0 values is shown in Tables IIa, b, where the differences taken from the values at 0° C. for three temperatures are compared with differences of ΔE_C , ΔS_C calculated for these temperatures by the above method. For the partial molal volume of He in water, we have the value of Michels, Gerver and Bijl⁶ of 16 c.c.; for the other gases, V is unknown but we take the Van der Waal's b value, as suggested by these authors, as a measure of V . Values of b used, in c.c. per mole are Ne 17.1, A 32.2, Kr 39.8, Xe 51.

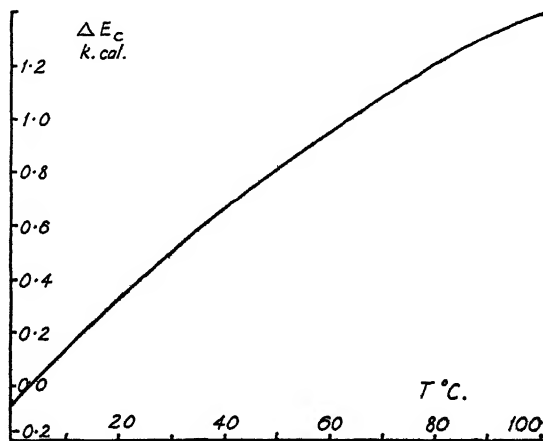


FIG. 2.

From equation (4a) we have that

$$\Delta E_A, T_2 = \Delta E_A, T_1 + k(T_2^2 - T_1^2) \frac{\partial}{\partial T} \ln \frac{f_S}{f_G}.$$

Considerations of section 6b and 6c suggest roughly that

$$\frac{\partial}{\partial T} \ln \frac{f_S}{f_G} \sim N \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G} \sim -0.008,$$

and so the maximum correction, at 353° K., to the above values is about 0.5 k.cal., small in comparison with the calculated ΔE_C .

Thus with the exception of He the temperature variation of ΔE^0 and ΔS^0 may be represented by variations in ΔE_C , ΔS_C . The large discrepancy for He may well be associated with the value of V used,

* At 4° C. ΔS_C equals zero. $\Delta E_C = pV = 2 \times 10^{-4}$ K. cal. mole⁻¹.

⁶ Michels, Gerver and Bijl, *Physica*, 1936, 3, 797.

which would appear to be anomalously large in comparison with its atomic radius. It is hoped to clear up this point later. In general, the calculated values are larger than the observed differences, but the general course of the variation is in agreement with the experimental fact and we can therefore write approximately,

$$\Delta E_T^0 = \Delta E_A + \Delta E_C, T,$$

$$\Delta S_T^0 = \Delta S_A + \Delta S_C, T.$$

Here ΔE_A , ΔS_A are roughly constant, and are strictly the values at 4° C., where $\Delta E_C, T$, $\Delta S_C, T$, are zero (little error is involved if we consider them as the values at 0° C.).

TABLE IIa.— $\delta E = \Delta E_T^0 - \Delta E_{273}^0$ (EXPTL.).

Gas.	293°K.		323.		353.	
	δE .	ΔE_C .	δE .	ΔE_C .	δE .	ΔE_C .
He	0.11	0.61	0.27	1.4	0.43	2.05
Ne	0.5	0.65	1.21	1.50	1.91	2.20
A	0.76	1.23	1.89	2.83	3.02	4.14
Kr	1.07	1.51	2.72	3.49	4.33	5.10
Xe	1.32	1.95	3.30	4.48	5.26	6.55

TABLE IIb.— $\delta S = \Delta S_T^0 - \Delta S_{273}^0$ (EXPTL.).

Gas.	293°K.		323.		353.	
	δS .	ΔS_C .	δS .	ΔS_C .	δS .	ΔS_C .
He	0.4	2.0	0.9	4.3	1.4	5.8
Ne	1.7	2.2	4.1	4.7	6.1	6.3
A	2.1	4.3	6.5	8.1	10.1	11.9
Kr	4.6	5.2	10.1	10.9	14.6	14.6
Xe	4.9	6.7	11.0	14.0	16.8	20.8

necessary amount with a small expenditure of energy because of the possibility of forming structures around the cavity in such a way as to compensate to some extent the hydrogen bonds broken in the expansion. The details of cavity formation in water and in organic solvents will be dealt with in a later paper.

5. Calculation of ΔE_{277}^0 .

In the equation $\Delta E_{277}^0 = \Delta E_{A, 277} + \Delta E_{C, 277}$, we are essentially concerned with $\Delta E_{A, 277}$. We consider an inert gas atom as just touching a water molecule, *i.e.*, with a separation of centres of $r_G + r_W$. There are three forces, the London forces (attraction), the polarisation of the gas atom in the field of the water dipole (attraction), and the repulsion forces. The interaction energy per water molecule, E_A , is

$$E_A = -\frac{\alpha_G \mu_W^2}{(r_G + r_W)^6} - \frac{3}{2} \cdot \frac{\alpha_G \alpha_W}{(r_G + r_W)^6} \cdot \frac{I_G I_W}{I_G + I_W} + \frac{b}{(r_G + r_W)^9} \quad (6)$$

(α = polarisability, I = ionisation potential, r = molecular radius). The repulsion constant b is evaluated by the condition $\partial E_A / \partial r = 0$ at $r = r_G + r_W$; μ_W , r_W are from Bernal and Fowler,⁷ α and I from London's paper.⁸

TABLE III.

Gas.	r_G , (Å).	$\alpha \cdot 10^{24}$ (cm. ³).	I , (e. vo.).	$b \times 10^{24}$.	$-E_A$, (K. cal.).	$\frac{\Delta E_{277}^0}{E_A}$.
He .	0.93	0.20	24.5	65.9	0.256	1.6
Ne .	1.12	0.39	21.5	154.4	0.166	10.9
A .	1.54	1.63	15.4	890	0.416	7.3
Kr .	1.69	2.46	13.3	1444	0.436	9.8
Xe .	1.90	4.00	11.5	2650	0.445	11.6

In Table II $\Delta E_{277}^0 / E_A$ gives the number of water molecules surrounding the gas atom for our calculation to give exact agreement with experiment. The average value is 10, a not unreasonable figure, since one can visualise suitable cavities in the water structure surrounded by 8 water molecules. Stereo-chemically it would not be possible to pack more than a limited number of waters round an He atom, because of its small size, and this is a feasible explanation of the anomalously low ratio given in the last column. This calculation is an argument in itself, that any cavity formation at 4° C. must have a negligible ΔE_G . If, as Lange and Watzel⁵ consider, we had to make a hole on a quasi-lattice point in water, involving $\Delta E_G \sim 10$ k.cal., into which we put a gas atom with the evolution of $-4E_A$,* i.e., about 1.5 k.cal., we should obtain $\Delta E^0 \sim 8.5$ k.cal., instead of the observed value of -4 k.cal.

6. The Calculation of ΔS_{277}^0 .

We first draw attention to Fig. 3, where values of ΔS_{298}^0 (i.e., at 25° C.) given by Butler⁹ (transposed to our standard states by $\Delta S^0 = \Delta S^0$ (Butler) + 29.4 - 8.4) are plotted against the quantity $3/2 R \ln m_G/m$, where m is the mass of the gas molecule and m_G is its reduced mass against a water molecule. Strictly it would be preferable to plot ΔS_{277}^0 , but this is not available, and ΔS_G , while appreciable, is not sufficiently so to be anything like the determining factor. The rare gases lie on a straight line, and such behaviour is to be expected theoretically where no appreciable restriction of the water in the field of the gas molecule occurs, and where the main change in entropy is to be associated with a simple loss of translation. The factor $3/2 R \ln m_G/m$ will arise in any partition functions constructed for the system, and is independent of any considerations of how the structure of the water will effect the concentration term in the partition function for the solution. The more negative values of ΔS^0 with the more complex gases indicates the presence of additional factors, for example, some loss of rotation on solution; but they might lie better if the ΔS_G terms

⁷ Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

⁸ London, *Trans. Faraday Soc.*, 1937, 33, 8.

* An inert gas atom on a quasi-lattice point will have four surrounding H₂O molecules.

⁹ Butler, *Trans. Faraday Soc.*, 1937, 33, 229.

had been subtracted, and these may be important in some instances. C_2H_6 shows a considerably smaller $-\Delta S^0$ which may arise from its well known chemical interaction with water. This graph encourages us to attempt the calculation of ΔS_{277}^0 in terms of simple translational factors.

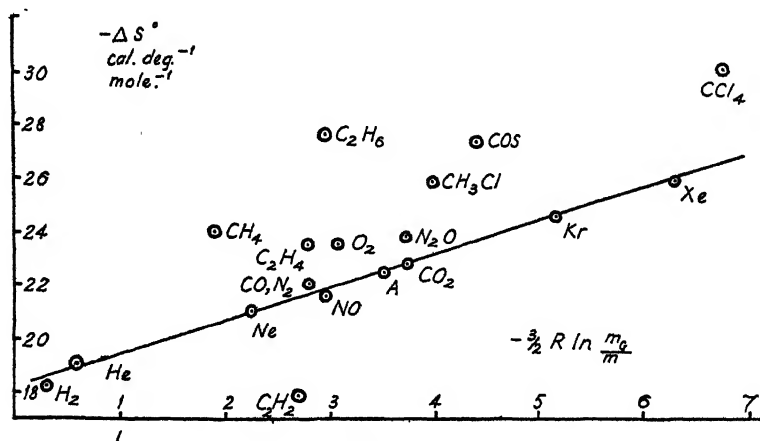


FIG. 3.

(a) The Partition Functions.

The entropy of 1 mole of gas at 1 atmosphere pressure in a volume V is

$$S_G^0 = Nk \left[\ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V}{N} + \frac{5}{2} \right]. \quad (7)$$

V is proportional to T and is 22.4×10^3 c.c. at 273° K.

In solution if we regard the N_W water molecules and N_G gas molecules as perfectly interchangeable on $N_W + N_G$ quasi-lattice points without seriously increasing the energy of the system then the partition function $f(T)$ for the system might be approximated by the formula of Guggenheim¹⁰

$$f(T) = f_W(T) f_G(T) \\ = \frac{(N_W + N_G)!}{N_W! N_G!} \left\{ V_W \frac{(2\pi m_W kT)^{3/2}}{h^3} \cdot J_W \right\}^{N_W} \left\{ V_G \frac{(2\pi m_G kT)^{3/2}}{h^3} \cdot J_G \right\}^{N_G} e^{-\frac{(N_W \epsilon_W + N_G \epsilon_G)}{kT}} \quad (8)$$

Here V denotes the free volume of the molecule, *i.e.*, the volume in which the molecule can move before building up a potential energy comparable with kT . J is the partition function for the internal energy of the molecule, while ϵ denotes the contribution of 1 molecule to the configurational potential energy of the solution. Configurational energy can be neglected for purposes of entropy and we omit this factor in what follows. We abbreviate

$$f(T) = \frac{(N_W + N_G)!}{N_W! N_G!} (\phi_W)^{N_W} (\phi_G)^{N_G} \quad (9)$$

¹⁰ Guggenheim, *Fowler's "Statistical Mechanics,"* 1936, 524.

The entropy of the solution is *

$$S(T) = k \left[\ln f(T) + T \frac{\partial}{\partial T} \ln f(T) \right] \quad (10)$$

The partial molal entropy of the gas in solution of concentration n_G moles in n_W moles water is defined by

$$\bar{S}_S = \left(\frac{\partial S(T)}{\partial n_G} \right)_{n_W, T, p} = N \left(\frac{\partial S(T)}{\partial N_G} \right)_{n_W, T, p} \quad (11)$$

Inserting the value of $f(T)$ by (9) in (10) and then differentiating according to (11) gives

$$\begin{aligned} \bar{S}_S = Nk \left[\ln \frac{N_W + N_G}{N_G} + \ln \phi_G + T \frac{\partial}{\partial T} \ln \phi_G \right] \\ + N_W k \left[\left(\frac{\partial \ln \phi_W}{\partial n_G} \right)_{n_W, T} + \left\{ T \frac{\partial}{\partial T} \ln \phi_W \right\}_{n_W, T} \right] \quad (12) \end{aligned}$$

To obtain the standard value \bar{S}_S^0 we merely insert values of N_W , N_G corresponding to a concentration of 1 mole per litre. Here the terms in the second bracket are taken as equal to ΔS_G , which we have already considered thermodynamically. So we may write (see equation 3b).

$$\bar{S}_{A, T}^0 = Nk \left[\ln \frac{N_W + N_G}{N_G} + \ln \phi_G + T \frac{\partial}{\partial T} \ln \phi_G \right] \quad (13)$$

The above partition functions will hold approximately for the inert gases in those organic solvents with a minimum of structure, but for water only in the region above about 200° C. We modify them as follows: at room temperature, we consider only certain points in the water structure as available for gas molecules. For a gas molecule to actually occupy a water quasi-lattice point would involve a ΔE_G comparable with the evaporation heat of water, and our energetic considerations have suggested that this does not occur. We may visualise the available points as cavities which can be easily enlarged to contain a gas molecule because of the possibility of water in the neighbourhood to form low energy structures. If there are N_H such cavities, or available sites, among which N_G gas molecules are distributed we now have $\frac{N_H!}{N_G! (N_H - N_G)!}$ physically distinct configurations, considerably less than the $\frac{(N_W + N_G)!}{N_W! N_G!}$ of equation (8). So

$$f(T) = \frac{N_H!}{N_G! (N_H - N_G)!} (\phi_W)^{N_W} (\phi_G)^{N_G} \quad (14)$$

In a similar way to the above

$$\bar{S}_{A, T}^0 = Nk \left[\ln \frac{N_H - N_G}{N_G} + \ln \phi_G + T \frac{\partial}{\partial T} \ln \phi_G + T \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G} \right] \quad (15)$$

* The energy is given by $E(T) = kT^2 \frac{\partial}{\partial T} \ln f(T)$ where, of course, the full partition function with configurational energy included is employed.

This presentation has the drawback that it does not easily lead, as it should, to equation (13) at high temperatures.* It should, however, approximately hold in the region of 4° C. Alternative forms will be considered in a later paper. In $T \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G}$ we have a term giving the influence of the change of structure of the water with temperature on the entropy of solution.

So for the entropy of solution at 277° K. by equation (3b), (7) and (15) (substituting for ϕ)

$$\Delta S^0 = \Delta S_C + R \left[\ln \frac{N_H - N_G}{N_G} + \frac{3}{2} \ln \frac{m_G}{m} + \ln \frac{V_G N}{V} + T \frac{\partial \ln V_G}{\partial T} + T \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G} - 1 \right] \quad (16)$$

(b) The Free Volume.

We require a value for V_G . We do not calculate this from potential curves defined by equation (6), since the results in Table III suggest

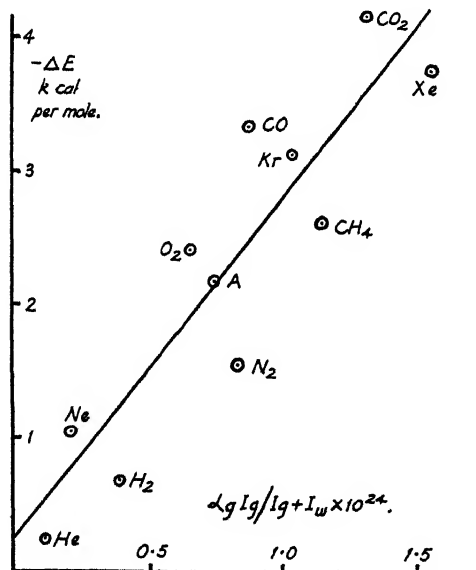


FIG. 4.

that this does not represent the actual state of affairs very accurately; a simpler method which is within the accuracy of our knowledge is as follows. To account for the experimental ΔE_{277}^0 in terms of a gas molecule in a cavity surrounded by a constant number of water molecules (which is the simplest picture to take), we have to correct our previous calculation in the gas-water separation r . We should not expect, for example, the water molecules to pack tightly around the smaller gas molecules, on stereochemical grounds. In Table III the variation in E_A over He to Xe is kept down by the increase in repulsion energy. Fig. 4,

where a rough linear relation between exptl. ΔE_{298}^0 † and $\alpha_G I_G / I_G + I_W$ (see equation 6) is seen to exist, for the inert gases would suggest that the cavity sizes are somewhat larger than $r_G + r_W$; in this case, we

* The term $\ln \frac{N_H - N_G}{N_G}$ holds only for the conditions that N_H is independent of N_G , since we can then neglect $\left(\frac{\partial N_H}{\partial N_G} \right) \cdot \ln \frac{N_H - N_G}{N_G}$. Where $N_H = N_G$ equation (14) leads to a term $\ln \frac{N_H}{N_G}$, but in this region the formulation (14) loses its significance, and is to be replaced by equation (9). We are here concerned only in roughly evaluating the concentration term at 4° C.

† Values from J. A. V. Butler.⁹

should obtain a greater effect of the dispersion forces, and the repulsion forces could be treated as a roughly constant percentage of the total energy as they would appear to be from the Figure. Polarisation forces can be neglected. At $r = r_G + r_W$ the repulsion forces are approximately equal to $-2E_A$. For the larger values of r visualised we might guess at a value of $-0.5 E_A$, the calculation is not very sensitive to the choice of repulsion energy in any case. If the gas molecules are surrounded by the reasonable number of 8 waters, then r^6 may be calculated from

$$\frac{1.5 \Delta E^0}{N} = -8 \cdot \frac{3}{2} \cdot \frac{\alpha_G \alpha_W}{r^6} \cdot \frac{I_G I_W}{I_G + I_W} \quad (17)$$

Treating the cavity as a sphere of volume $\frac{4}{3}\pi(r - r_W)^3$ then the free volume is

$$V_G = \frac{4}{3}\pi(r - r_W)^3 - \frac{4}{3}\pi r_G^3 \quad (18)$$

Since V/N for the molecules in the gas phase is 3.7×10^{-20} c.c. we can construct the following table.

TABLE IV.

Gas.	ΔE_{773}^0 (k. cal.).	$r - r_W$ (Å).	$V_G \times 10^{23}$ (cc.).	$R \ln \frac{V_G N}{V}$ (cal. deg ⁻¹ mole ⁻¹).
He . .	0.44	1.92	2.63	-14.5
Ne . .	1.95	1.39	0.54	-17.7
A . .	3.19	1.86	1.16	-16.1
Kr . .	4.53	1.85	0.63	-17.4
Xe . .	5.44	2.05	0.84	-16.8

The value of V_G is larger than the average value for pure organic liquids derived by Eyring and Kincaid,¹¹ of 0.5×10^{-24} c.c. The difference corresponds to 6 entropy units.

(c) Numerical Results.

We proceed to calculate equation (16). If in 55.5 moles of water (1 litre) there is 1 site per 20 water molecules, $\ln \frac{N_H - N_G}{N_G} = 0.57$. At present we have no evidence for this choice, other than that the general water picture of Bernal and Fowler⁷ would suggest suitable cavities might occur rather less than 1 in 10. Water becomes close-packed in the region of 200° C. and in this temperature range, all these available sites disappear, and so we can estimate $T \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G} \sim -2.1$. In the region of room temperature V_G will mainly depend upon the expansion coefficient of water, and so $\frac{T \partial \ln V_G}{\partial T}$ is negligible. So we can derive equation (24) and tabulate values for ΔS_{277}^0 . We have used

¹¹ Kincaid and Eyring, *J. Chem. Physics*, 1938, 6, 620.

values of V_G calculated at 273° A. since these are almost identical with those at 277° A.

$$\Delta S_{277}^0 = \Delta S_{C, 277} + R \left[-2.5 + \frac{3}{2} \ln \frac{m_G}{m} + \ln \frac{V_G N}{V} \right] \quad (19)$$

where $\Delta S_{C, 277} = 0.0 \text{ cal. deg.}^{-1} \text{ mole.}^{-1}$

TABLE V.

Gas.	$3/2 R \ln \frac{m_G}{m}$	$R \ln \frac{V_G N}{V}$	$-\Delta S^\circ$ calc.	$-\Delta S^\circ$ exptl.
He . .	-0.6	-14.5	20.2	18.9
Ne . .	-2.2	-17.7	25.0	22.5
A . .	-3.5	-16.1	24.7	25.0
Kr . .	-5.2	-17.4	27.7	28.7
Xe . .	-6.3	-16.8	28.2	30.2

Firstly, the rather good agreement in absolute value is better than we might justifiably expect, since the evaluation of equation (16) is speculative, not least in the calculation of V_G . However, the high values of V_G obtained are consistent with the theory of special, easily formed, cavities, into which solution occurs. If the gas molecules occupied quasi-lattice points of the water, we should approximate ΔS_C , which is the change in entropy of the water molecules surrounding a stationary hole on a quasi-lattice point, by L/T —translational contribution, *i.e.*, approximately $39 - 26 = 13$ e.u. (L = Latent heat of evaporation), and use equation (13). With any reasonable value of V_G (*i.e.*, $\sim 10^{-24}$ c.c.) we should obtain no agreement with experiment. Secondly, it is clear that at any rate 50 % of the variation in ΔS° over He to Xe can be attributed to the mass term.

The rather queer fluctuations in the intermediate values are due to our calculation of V_G which contains many uncertain factors; at present, we are really only justified in taking a constant value of -16.5 entropy units from this source. A comparison of the first and last columns of Table V would suggest that there is really a continuous change in the V_G factor of about -5.0 e.u., over He to Xe. (A part of this -5.0 e.u. might arise, however, from the restriction on the motions of water molecules in the walls of the cavity brought about by the force-field of the gas atom).

Solubility in Water at High Temperature.

At 80° C. for the inert gases and others $\Delta E_G \sim -\Delta E_A$ and $\Delta E^0 \sim 0$. For a 10 c.c. "molal cavity" at 200° C. $\Delta E_G \sim 2.15$ k.cal. and since we can safely assume no large increase in ΔE_A , ΔE^0 will now be positive. Such a reversal of temperature coefficient has been established by Wiebe and Gaddy,¹² and Saddington and Krase¹³ on the systems N_2/H_2O and H_2/H_2O . At these temperatures, the gas molecules share the quasi-lattice points of water equally with the water molecules and water now behaves in a similar way to organic solvents at more normal temperatures.

¹² Wiebe and Gaddy, *J. Amer. Chem. Soc.*, 1934, **56**, 76; 1933, **55**, 947.

¹³ Saddington and Krase, *ibid.*, 1934, **56**, 353; see also *Landolt-Bornstein*, Erg IIIa, 686.

Summary.

The energy and entropy of solution of an inert gas molecule in water can be accounted for by two consecutive processes:

- (a) the formation of a cavity;
- (b) the gas molecule enters the cavity.

The anomalous factors in the solubility of the inert gases in water, *e.g.* the negative temperature coefficient and its rapid increase to zero as the temperature is raised to 80° C., is to be explained mainly by the energy and entropy associated with process (a), which have been calculated thermodynamically. The energy and entropy of cavity formation are zero at 4° C., but increase strongly with increase of temperature.

A calculation of the energy of solution has been made from a simple model. An approximate partition function has been constructed which takes into account the influence of the water structure on the solution, and from it the entropy of solution has been calculated, and the main factors for the inert gases has been shown to be the loss of translational movement, and the entropy associated with cavity formation. The positive temperature coefficient observed for some gases in water above 100° C. is to be explained by the large energy required to form a cavity at these temperatures, which outweighs the solute-solvent attraction.

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THE CAPILLARY PROPERTIES OF α -AMINO-ACIDS.

By J. W. BELTON.

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The study of the capillary properties of the simple amino-acids is of interest in that the surface tension-concentration curve shows a marked variation with the length of the acid chain, and so with the moment of the dipolar ion present. The curves found for glycine and alanine are positive in slope, but those for amino-butyric and higher acids are negative; and in the investigation described below it is shown that this variation is still more marked in the presence of electrolytes, and depends on the amount of electrolyte present. The interaction of amino-acids and salts is well shown by their solubility relationships. Such interaction occurs in the surface phase, and the structure of the adsorbed film may be considerably modified by the presence of ions. A striking example is that of alanine solutions, at the surface of which water is positively adsorbed, but when electrolyte is added the acid is also pushed into the surface layer.

The effect of the addition of sodium chloride on the surface tension of glycine solutions has been noted by Lewis and Jones¹ who found an increase between pH 3 and pH 8.

Experimental.

The surface tensions were measured by the modification of the maximum bubble pressure method described by the writer in a previous paper,² where experimental details will be found. The jet used in the present investigation was 0.0128 cm. in radius; this figure was checked by standardisation with pure water and pure benzene. The glycine-hydrochloric acid solutions were made up by weight from a stock solution of the latter and solid glycine; the other solutions were made up by weight from the solids and pure water of surface tension 72.01 dynes/cm. The salt was of analar grade and the acids recrystallised specimens, which analysed as 100%. All the measurements were made at 25° C.

TABLE I.

m .	h .	γ .	k .
Glycine.			
0.502	10.965	72.54	1.06
1.005	11.055	73.11	1.10
1.507	11.15	73.74	1.15
2.009	11.215	74.18	1.09
Alanine.			
0.502	10.975	72.54	1.06
1.005	11.02	72.90	0.89
1.338	11.055	73.11	0.86
α-Amino-Butyric Acid.			
0.506	10.87	71.91	-0.20
1.002	10.85	71.78	-0.23
1.504	10.795	71.40	-0.40
Valine.			
0.420	10.61	70.18	-4.36

The Surface Tensions of Amino-Acid Solutions.

The results for binary solutions are shown in Table I, which gives the concentration of the acid in moles per 1000 g. of water, the maximum bubble pressure (h) in cm. of butyl phthalate, the surface tension (γ) and the value of k defined by the relation $\gamma = \gamma_0 + km$. The plot of γ against m gives a straight line in the case of glycine, but bends slightly toward the m -axis in the case of alanine and α -amino-butyric acid. These curves show that $d\gamma/dm$ decreases with the length of the acid chain and that it is positive for glycine

and alanine, but negative for α -amino-butyric acid and valine. The values of γ appear to be rather higher than those recently recorded by Pappenheimer, Lepie and Wyman.³

The Surface Tensions of Amino-Acid-Sodium Chloride Solutions.

The surface tensions of glycine, alanine, α -amino-butyric acid and valine solutions were measured in the presence of sodium chloride at various concentrations. As valine is not very soluble the measurements in its case were restricted to a series with one acid concentration, but for the other acids the acid concentration was varied as well as that of the salt. Table II gives the concentration of acid (m_2) and of salt (m_3) in moles per 1000 g. of water, the maximum bubble pressure (h) and the surface tension (γ) in dynes per cm.

¹ Jones and Lewis, *Biochem. J.*, 1932, 26, 638.

² Belton, *Trans. Faraday Soc.*, 1935, 31, 1413.

³ Pappenheimer, Lepie and Wyman, *J. Amer. Chem. Soc.*, 1936, 58, 1851.

The values of $(\partial\gamma/\partial m_2)_{m_3}$ and $(\partial\gamma/\partial m_3)_{m_2}$ have not been tabulated as it is much easier to see their general relations from graphs (Fig. 1). As the length of the acid chain increases $(\partial\gamma/\partial m_3)_{m_2}$ falls; for glycine it is constant and positive and has the same value as in binary sodium chloride solutions; for alanine it falls with increasing acid concentration and the $\gamma - m$ curves converge; for α -amino-butyric acid the fall is more marked and γ is less for the strong acid solutions than for the more dilute. The behaviour in the case of valine is curious; the surface tension reaches a maximum value for 2 M. salt, above which concentration valine is salted

TABLE II.

m_2	m_3	h	γ	m_2	m_3	h	γ
Glycine.				Alanine.			
0.502	1.002	11.225	74.25	0.502	1.002	11.205	74.11
1.005	1.024	11.315	74.86	1.005	1.024	11.265	74.51
1.507	1.047	11.41	75.48	1.338	1.039	11.295	74.71
2.009	1.070	11.48	75.93	0.502	2.051	11.44	75.66
0.502	2.051	11.465	75.83	1.005	2.096	11.50	76.07
1.005	2.096	11.58	76.60	1.338	2.127	11.515	76.18
1.507	2.142	11.67	77.20	0.502	3.077	11.725	77.57
2.009	2.190	11.75	77.73	1.005	3.145	11.735	77.62
0.502	3.077	11.735	77.62	1.338	3.191	11.75	77.73
1.005	3.145	11.845	78.36	0.502	4.102	11.96	79.13
1.507	3.213	11.935	78.95	1.005	4.193	11.96	79.13
2.009	3.284	12.00	79.38	1.338	4.255	11.96	79.13
0.507	4.102	11.99	79.27	α-Amino-Butyric Acid.			
1.005	4.193	12.10	80.04	0.506	1.039	11.11	73.48
1.507	4.284	12.165	80.45	1.002	1.039	11.05	73.08
2.009	4.378	12.27	81.16	1.504	1.042	10.94	72.88
0.502	S'turt'd.	12.545	82.17	0.506	2.115	11.33	74.94
1.005		12.615	83.47	1.002	2.117	11.21	74.15
1.507		12.695	83.98	1.504	2.120	11.05	73.08
2.009		12.76	84.42	0.506	3.228	11.54	76.33
Saturated.	1.070	11.69	77.34	1.002	3.232	11.35	75.08
"	2.190	11.975	79.22	1.504	3.220	11.14	73.67
"	3.213	12.21	80.76	0.506	4.383	11.75	77.73
"	4.378	12.50	82.68	1.002	4.405	11.50	76.07
				1.504	4.361	11.20	74.08
				Valine.			
				0.42	1.04	10.75	71.12
				0.42	2.11	10.82	71.56
				0.42	3.22	10.825	71.59
				Sat.	4.33	10.825	71.59

out, and in spite of the addition of sodium chloride, which one would expect to increase the surface tension, and of the salting out of valine which should also increase it, the surface tension remains constant. The values of $(\partial\gamma/\partial m_2)_{m_3}$ also vary with the length of the acid chain; for glycine it is constant and independent of the salt concentration; for alanine it is less than for glycine and falls with increasing salt concentration, until for 4 M. salt it is zero; for α -amino-butyric acid it is negative and falls with increasing salt concentration; while valine gives still lower values which fall even more quickly with salt concentration. This effect of the length of the acid chain is probably bound up with the moment of

the molecule, the number of zwitterions present in the solution and the consequent modification of the surface structure by the presence of ions.

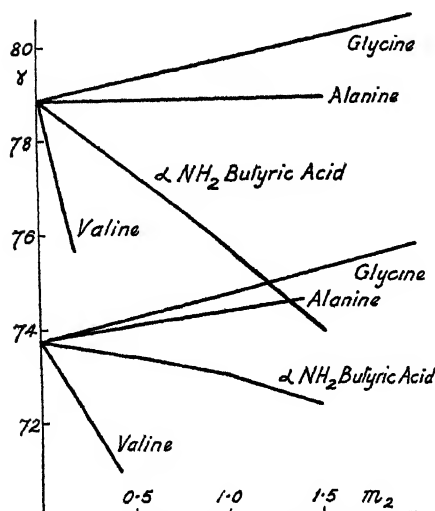


FIG. 1.—Amino Acid—Salt Solutions
 γ — m^2 .

Upper curves 4 M. NaCl.
Lower curves 1 M. NaCl.

The Surface Structure of α -Amino-Acid Salt Solutions.

The surface tensions of sodium chloride solutions increase with concentration and in consequence thermodynamic considerations demand that the solute is negatively adsorbed at the surface. We may assume that for α -amino-acid-salt solutions the surface layer will consist either of water only or of water and acid. The surface concentrations of these components may be calculated from the Gibbs equation, according to which

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3$$

where μ is the chemical potential and the subscripts refer to water, acid and salt respectively. If the adsorption of salt is zero at the dividing surface, the last term disappears. According to the Duhem-Margules equation

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 = 0$$

from which
$$d\gamma = \Gamma_1 \left(\frac{n_2}{n_1} d\mu_1 + \frac{n_3}{n_1} d\mu_3 \right) - \Gamma_2 d\mu_3.$$

Thus

$$\left(\frac{\partial \gamma}{\partial m_2} \right)_{m_3} = \Gamma_1 \frac{n_2}{n_1} RT \left[\left(\frac{\partial \ln f_2}{\partial m_2} \right)_{m_3} + \frac{1}{m_2} \right] + \Gamma_1 \frac{n_3}{n_1} RT \left(\frac{\partial \ln f_2}{\partial m_2} \right)_{m_3} - \Gamma_2 RT \left(\frac{\partial \ln f_3}{\partial m_2} \right)_{m_3}$$

and

$$\left(\frac{\partial \gamma}{\partial m_3} \right)_{m_2} = \Gamma_1 \frac{n_2}{n_1} RT \left(\frac{\partial \ln f_2}{\partial m_3} \right)_{m_2} + \Gamma_2 \frac{n_3}{n_1} RT \left[\left(\frac{\partial \ln f_2}{\partial m_3} \right)_{m_2} + \frac{1}{m_3} \right] - \Gamma_2 RT \left[\left(\frac{\partial \ln f_3}{\partial m_3} \right)_{m_2} + \frac{1}{m_3} \right].$$

Solution of these two equations gives

$$\Gamma_1 = \frac{\left(\frac{\partial \gamma}{\partial m_2} \right)_{m_3} \left(\frac{\partial \ln f_2}{\partial m_3} \right)_{m_2} - \left(\frac{\partial \gamma}{\partial m_3} \right)_{m_2} \left[\left(\frac{\partial \ln f_2}{\partial m_2} \right)_{m_3} + \frac{1}{m_2} \right]}{\frac{n_3}{n_1} RT \left[\left(\frac{\partial \ln f_2}{\partial m_3} \right)_{m_2} \left(\frac{\partial \ln f_3}{\partial m_2} \right)_{m_3} - \left[\left(\frac{\partial \ln f_3}{\partial m_2} \right)_{m_3} + \frac{1}{m_3} \right] \left[\left(\frac{\partial \ln f_2}{\partial m_3} \right)_{m_2} + \frac{1}{m_2} \right] \right]}$$

$$\Gamma_2 = - \frac{\frac{1}{RT} \left(\frac{\partial \gamma}{\partial m_2} \right)_{m_3} - \frac{\Gamma_1}{n_1} \left[\left[\left(\frac{\partial \ln f_2}{\partial m_2} \right)_{m_3} + \frac{1}{m_2} \right] + 2n_3 \left(\frac{\partial \ln f_3}{\partial m_2} \right)_{m_3} \right]}{\left(\frac{\partial \ln f_2}{\partial m_2} \right)_{m_3} + \frac{1}{m_2}}$$

The E.M.F.s of cells without transference containing various amino-acids and sodium chloride have been measured by Joseph⁴ who gives values for $\ln f_3/a_3$ and $\delta \ln f_2/\delta m_3$ where a_3 is the activity coefficient in the isomolal salt solution. From these data, from the relation

$$\frac{\delta \ln f_2}{\delta m_3} = \nu \frac{\delta \ln f_3}{\delta m_2},$$

shown by Bjerrum⁵ to hold for such solutions, and from the known variation of a_3 with salt concentration, it is possible to calculate $\delta \ln f_2/\delta m_3$, $\delta \ln f_2/\delta m_2$, $\delta \ln f_3/\delta m_3$ and $\delta \ln f_3/\delta m_2$. The values of $(\partial \gamma/\partial m_2)_{m_3}$ and $(\partial \gamma/\partial m_3)_{m_2}$ may be obtained graphically from the data in the previous section. The surface concentrations calculated in this way are given in Table III.

At the surface of the glycine-salt solutions there is a deficiency of glycine, but an excess of water molecules, which, assuming the area of a water molecule to be 7\AA^2 , corresponds to fewer than can be accommodated in a uni-molecular layer. The number of water molecules adsorbed is in all cases less than for the isomolal salt solution, and falls with both increasing acid and increasing salt content; at high salt concentrations the effect of acid on the water adsorption is small. The surface deficiency of glycine increases with acid concentration, and is affected very little by salt.

In the case of alanine and α -amino-butyric acid both water and acid molecules are adsorbed at the surface; the fraction (x) of the surface occupied by water and the space left ($1 - x$) for the accommodation of acid molecules have been calculated from the known area of the water molecule and are given in the table. For alanine, both the free space and the number of acid molecules adsorbed increase linearly with the salt concentration up to 3 M. The water adsorption decreases with the salt

TABLE III.

m_2	m_3	Γ_1	Γ_2	x	$1 - x$
Glycine.					
0.5	1	18.5	0.045		
1.0	1	18.5	0.099		
1.5	1	17.5	0.18		
2.0	1	17.7	0.26		
0.5	2	16.8	0.43		
1.0	2	16.8	0.085		
1.5	2	16.2	0.14		
2.0	2	16.1	0.19		
0.5	3	14.8	0.051		
1.0	3	14.8	0.10		
1.5	3	14.3	0.17		
2.0	3	14.2	0.23		
0.5	4	13.6	0.040		
1.0	4	13.6	0.080		
1.5	4	13.1	0.13		
2.0	4	13.0	0.18		

Alanine.

0.5	1	18.1	0.037	0.77	0.23
1.0	1	16.9	0.089	0.72	0.28
1.34	1	16.0	0.12	0.68	0.32
0.5	2	16.4	0.060	0.70	0.30
1.0	2	15.4	0.17	0.65	0.35
1.34	2	14.5	0.20	0.62	0.38
0.5	3	14.5	0.089	0.62	0.38
1.0	3	13.6	0.22	0.58	0.42
1.34	3	12.9	0.32	0.55	0.45
0.5	4	13.3	0.13	0.56	0.44
1.0	4	12.4	0.24	0.53	0.47
1.34	4	11.8	0.30	0.50	0.50

 α -Amino Butyric Acid.

0.5	1	16.5	0.31	0.70	0.30
1.0	1	13.3	0.75	0.56	0.44
1.5	1	10.2	1.30	0.43	0.57
0.5	2	13.6	0.42	0.57	0.43
1.0	2	10.1	0.87	0.43	0.57
1.5	2	7.3	1.43	0.31	0.69
0.5	3	11.7	0.57	0.50	0.50
1.0	3	8.6	1.18	0.36	0.64
1.5	3	5.7	1.81	0.24	0.76
0.5	4	10.7	0.76	0.45	0.55
1.0	4	8.0	1.36	0.34	0.66
1.5	4	4.9	2.21	0.24	0.76

Valine.

0.42	1	13.3	2.4		
0.42	2	6.1	1.6		

⁴ Joseph, *J. Biol. Chem.*, 1935, **111**, 489.⁵ Bjerrum, *Z. physik. Chem.*, 1923, **104**, 405.

content and is below that for the isomolal salt solution; the variations produced are very similar to those for glycine except that this acid has a greater effect. The plot of Γ_2 against m_3 for different acid concentrations gives a series of curves which converge towards the origin, showing that there is no adsorption of acid in the absence of salt, which is in agreement with the fact that dy/dm_2 is positive for pure alanine solutions. It appears that as the water molecules are removed from the surface by the action of salt, amino-acid molecules take their place.

Amino-butyric acid shows a similar behaviour. The space available for amino-acid and the number of amino-acid molecules adsorbed vary linearly with the salt content up to 3 M. The water adsorption is less than for alanine, but that of the acid is greater. The curves for different acid concentrations given by the plot of Γ_2 against m_3 , do not pass through the origin, but intercept the Γ_2 axis at positive values of Γ_2 , corresponding to the adsorption of acid in solutions containing no salt; this is in agreement with the observed negative values of dy/dm for such solutions.

Summary.

Measurements have been made of the surface tensions of (a) aqueous solutions of glycine, alanine, α -amino-butyric acid and valine, and (b) solutions of these acids with the addition of sodium chloride in varying amounts. The slope of the surface tension-concentration curve varies with the length of the hydrocarbon chain and this variation becomes more marked in the presence of salt. The effect of sodium chloride on the surface layer is discussed, and it is shown that in the case of alanine salt changes the sign of the acid adsorption from negative to positive.

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THE CATALYSED POLYMERISATION OF BUTADIENE AT A LIQUID-GAS INTERFACE.

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Experiments on the homogeneous polymerisation of vinyl derivatives both in the gas and liquid phase have now progressed to a stage where it is possible to gain some idea of the mechanisms of the reactions by means of suitable kinetic analysis. In many reactions, of course, all that can be done is to determine the kinetic order of the reactions making up the polymeric process, so that guidance may be given to a choice of the actual chemical reaction involved. Besides homogeneous polymerisation, it has been found that interfacial polymerisation occurs quite as readily in a suitable environment. For example, butadiene, vinyl chloride, methylmethacrylate all polymerise easily when dispersed to form an emulsion. Practically nothing, however, is known about the mechanism of the reaction; in fact it is difficult to say whether polymerisation occurs at the interface, in the monomer or in the dispersion medium.

The work described in the present paper is an attempt to see what can be done in the application of kinetic methods of analysis to the polymerisation of butadiene vapour on the surface of aqueous hydrogen peroxide solutions. That the polymerisation does not occur in the liquid nor in the gas phase is shown by the following experiments. On prolonged contact of the butadiene with the hydrogen peroxide a slight cloudiness is observed in the hydrogen peroxide, which demonstrates that polymerisation can indeed occur in the solution. The velocity of this liquid phase reaction, however, is so small that it cannot have any effect on the surface tension of the hydrogen peroxide under the conditions in which this property is used to study the interface polymerisation in the experiments described below. Under the conditions of temperature and pressure used in the interface polymerisation, photochemical polymerisation in the gas phase indicates a chain length of the reaction so small that there is little reason to suppose that any sensible amount of gas phase polymerisation accompanies the interface reaction. Thus it seems reasonable to suppose that the reaction investigated by the experimental technique described below is confined to the interface.

There are in principle two methods whereby the polymerisation could be followed. The first consists in measuring the rate of disappearance of the butadiene and the second in observing the change in some property of the interface. Since the area of the interface used must remain substantially constant during the reaction it is evident that a plane liquid surface must be used. This, however, introduces the difficulty that the number of polymer molecules which can be packed into such an interface is so small that the amount of butadiene which would disappear from the gas phase could not be conveniently measured. The second method must therefore be used and the surface property which is most easily measured is surface tension. This technique will only be applicable if, by suitable calibration experiments, a relation is established between the change in surface tension at such an interface and the surface concentration of the polymer.

Apparatus.

The ring method of measuring surface tension was deemed most suitable for the present purpose. An apparatus was therefore devised in which a constant pressure of butadiene up to several atmospheres could be maintained above a water surface, the surface tension of which could be measured at intervals. The design adopted is shown in Fig. 1.

The reaction vessel is a flanged brass cylinder 8" deep \times 6" diameter with a brass cap secured by eight thumb screws and jointed by means of a thick rubber ring. This vessel is immersed in a thermostat to just below the flange. The aqueous hydrogen peroxide is contained in a glass dish standing on a platform A, and surface tension measurements can be made by means of the platinum ring B, suspended from the spring C. The spring can be raised and lowered from outside the case by means of a screw and plug movement, drawn in detail in Fig. 1A. The inverted taper plug D is accurately ground into the socket E and is rotated by the external knob F. The rod G, which carries the spring, is prevented from rotating by a pin H, fitted into a slot cut in the rod. The plug is held in its seating by means of a small compression spring. It will be observed that rotation of the knob F will produce only a vertical movement of the spring C. The movement of the ring is measured by means of an optical lever; a beam of light passes through the window N and is reflected from the pivoted mirror J on to a scale K, so that the position of the spot of light on the scale gives a measure—not necessarily linear—of the height of the ring. The position

of the top of the spring can be read off from the rotation of the knob F which is graduated. If now the ring is supposed to be hanging in the air and the spring is raised progressively a curve can be constructed showing the scale reading as a function of the movement of knob F, and thus of the height h_0 of the top of the spring. Next suppose the ring to be put into the water surface and the raising of the spring repeated; a second curve can be drawn and will clearly not coincide with the first since now the ring is held by the surface. Now it is known that the scale reading is a measure of the position of the ring, so that the difference between the heights h_0 and h of the top of the spring in the two experiments, compared at any constant scale reading, gives the extension of the spring. A further curve can therefore be constructed in which $(h_0 - h)$ is drawn as a function of any convenient parameter: h_0 has actually been used, and it is found that the extension $(h_0 - h)$ increases to a maximum at the break point. This maximum value is easily found by a short extrapolation. Further, assuming the spring to obey Hooke's Law, the tension in the spring is proportional to the extension and so the maximum extension gives a linear measure of the surface tension of the liquid. The constant of proportionality is easily obtained by measuring the extension for the surface of clean water, of which the surface tension is known.

In order to carry out a series of these "weighings" of the ring alternately in air and in water, it is necessary to have a method of raising and lowering the vessel of water. For this purpose the platform A is capable of vertical movement in a socket L and is moved by a pivoted lever M, which in turn can be

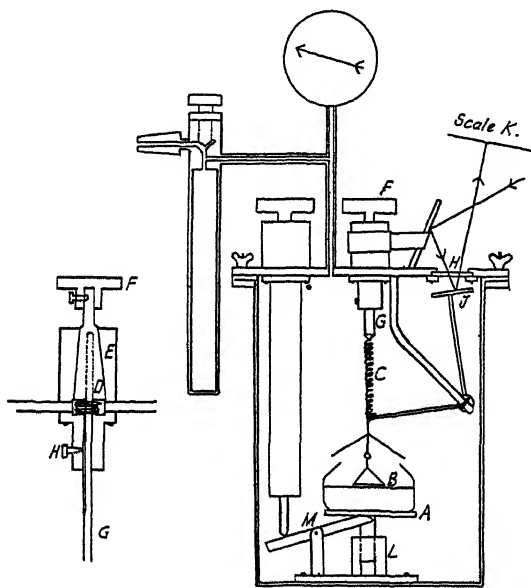


FIG. 1A.

FIG. 1.—Apparatus.

adjusted from outside the case by a movement similar to that sketched in Fig. 1A. In order to prevent any contamination of the water surface a conical screen is suspended over the glass dish, the top of which is also contracted.

Butadiene is admitted via a side tube fitted with a screw valve so arranged as to leave the side tube always in communication with the cylinder. Butadiene is condensed in a side tube by cooling in liquid air. The valve is then shut and the side tube placed in a small thermostat, the temperature of which controls the pressure of butadiene supplied to the cylinder. Some butadiene remains as liquid in the side tube. A Bourdon gauge gives a direct reading of the butadiene pressure. Before an experiment the cylinder is roughly evacuated by a water pump so that the pressure read is that of butadiene and water vapour from which the nett butadiene pressure is known.

One difficulty encountered was to find a suitable lubricant for the taper plugs, since these had to be vacuum tight and pressure tight at 60°–80° C.

and yet capable of rotation. A red wax, rather softer than picein, mixed with graphite was finally adopted.

Trouble was experienced from water condensing on the window and on the mirror J. This was avoided by the use of a small electric radiator to heat the top of the cylinder sufficiently to prevent condensation.

Some experiments were also done with the following arrangements. On pumping out the cylinder with the glass dish already containing the hydrogen peroxide, some concentration of the solution may occur. An arrangement was therefore constructed inside the cylinder to hold a sealed tube of air free hydrogen peroxide. The end of the tube was drawn off to a fine spike of glass projecting over the edge of the glass dish. By means of a movable glass knife the spike was broken to allow the contents of the tube to enter the dish after the evacuation of the cylinder. After a number of trials with this more laborious method, however, it was discontinued, because the results were not sensibly different from those employing the simpler technique.

A typical experiment was carried out as follows. The glass dish and platinum ring were cleaned with chromic acid and well washed, the ring being afterwards heated in a flame. The conical screen was washed with benzene and dried by warming, followed by heating. The hydrogen peroxide was preheated to 60° C., 100 c.c. placed in the dish which stood on the platform, the cylinder head mounted and screwed down. With the platform lowered, the ring was "weighed" in air (*i.e.*, the curve scale reading $\sim h_0$ constructed). The platform was then raised to bring the ring into the water and its height adjusted until the scale reading was the same as the initial reading for the ring in air. The ring was then "weighed" again. These two sets of readings give the data from which the surface tension is to be calculated. For water, the surface tension at 60° C. is taken as 66.2 dynes/cm. The apparatus was evacuated, and then the required pressure of butadiene introduced. Surface tension readings were taken as soon as the pressure rose and thereafter at intervals for the remainder of the day, with a final reading the following morning.

Under the above mentioned conditions, however, hydrogen peroxide is known to be unstable unless some inhibitor is added to the solution. Some knowledge was therefore required about the stability of these solutions so that optimum conditions for stability could be found. In addition it was necessary to be able to prepare a solution which would decompose in a time somewhat shorter than the time of reaction, so that an approximate estimate could be made of the life-time of the active polymer.

Hydrogen peroxide made from barium peroxide and sulphuric acid, proved rather unstable even in the presence of slight excess of acid. This may have been due to the presence of finely divided barium sulphate. Experiments were then made with solutions prepared from sodium peroxide and hydrochloric acid. Again large differences in decomposition rate were observed but acid solutions were comparatively stable. Finally, about 14 volumes solution was prepared by the vacuum distillation of the commercial 20 volumes solution. This, too, was unstable at 70° C., unless the pH value of the solution was decreased to quite a low value by the addition of sulphuric acid. The following figures show how the rate of decomposition which follows a first order course, varies with the concentration of added acid. The time of reaction, 18-19 hours, is considerably greater than that employed for the polymerisation of butadiene.

Although the results with the higher concentrations of acid are not very reproducible, yet it can be seen that there is a marked stabilising effect of the acid above a concentration $N. \times 10^{-2}$. Moreover, under these conditions the stability is such as to permit the carrying through of polymerisation experiments in a matter of six hours, when the fall in concentration is about 5%. The majority of the experiments were therefore carried out with hydrogen peroxide stabilised in this manner, the assumption being made that the added acid has no effect on the course of the polymerisation.

TEMPERATURE 70° C.

1st Series.		2nd Series.	
Acid Concentration (N.).	% H ₂ O ₂ Decomposed in 19 Hours.	Acid Concentration (N.).	% H ₂ O ₂ Decomposed in 18 Hours.
0	100	0	100
5 × 10 ⁻⁴	100	1 × 10 ⁻²	21.9
1 × 10 ⁻³	95	2 × 10 ⁻²	23.8
2 × 10 ⁻³	24	4 × 10 ⁻²	25.6
4 × 10 ⁻³	37	7.7 × 10 ⁻²	30.8
1 × 10 ⁻²	34	1.43 × 10 ⁻¹	39.5

The butadiene was kindly supplied, compressed in cylinders, by Imperial Chemical Industries Ltd. (Dyestuffs Group). The butadiene content was 99 %.

Experimental Results.

The parameters which may be varied for the purpose of determining the mechanism of the reaction are (a) the pressure of butadiene, (b) concentration and stability of the catalyst, (c) temperature. As the following typical figures show, the surface tension of the hydrogen peroxide is reduced quickly when the butadiene is admitted to the vessel. This undoubtedly is due to adsorption of butadiene. The initial drop is followed by a gradual decrease to a constant value owing to polymerisation at the interface. It is fortunate that there is such a two-stage drop in surface tension for it allows of the determination of the adsorption isotherms of butadiene on such hydrogen peroxide solutions. The measurement cannot easily be carried out on strong solutions since the polymerisation rate is too high.

Table I gives a typical example of the data obtained during a polymerisation run on one volume hydrogen peroxide.

TABLE I.

Time, Hours.	$h_0 - h$ Maximum mms.	Pressure Butadiene lbs./sq. in.	σ , $-\Delta\sigma$, $-\Delta\sigma$ Dynes per cm. (Polymer).		
			σ	$-\Delta\sigma$	$-\Delta\sigma$
—	3.23	—	66.2	—	—
0	2.82	36	57.8	8.4	0.1
0.5	2.63	45.5	54.0	12.2	1.5
1.0	2.54	48	52.0	14.2	2.9
1.75	2.35	49	48.2	18.0	6.5
2.75	2.06	49	42.2	24.0	12.5
3.75	1.95	49	40.0	26.2	14.7
5.0	1.74	49	35.7	30.5	19.0
6.0	1.69	49	34.7	31.5	20.0
7.0	1.64	49	33.6	32.6	21.1
24.0	1.45	49	29.8	36.4	24.9

Desorption curves were obtained after some experiments. The side tube temperature was lowered in stages, so that the butadiene pressure fell, and the surface tension measured. In all these cases it was found that, within experimental error, the desorption curve was parallel to the

adsorption curve. That is to say, the butadiene made the same contribution to the surface tension lowering whether polymer was present or not. The contribution of the butadiene could thus be subtracted from the measured $-\Delta\sigma$ and the polymer contribution obtained separately. The last column of the above table was obtained in this way.

In Fig. 2 are given the experimental data on the adsorption of butadiene at 50° and 60° C. on 1 volume hydrogen peroxide, while Fig. 3 and Tables II and III summarise the experiments on the rate of polymerisation as a function of temperature or pressure (for method of calculation, see below).

By utilising the adsorption curves the heat of desorption of butadiene may be calculated in the following way. From the Gibbs' equation

$$\Gamma = \frac{p}{RT} \cdot \frac{d\sigma}{dp}$$

where Γ is the surface concentration of the butadiene, the heat of desorption E is simply given by

$$\ln \frac{\Gamma_{T_1}}{\Gamma_{T_2}} = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where Γ_{T_1} and Γ_{T_2} are the adsorptions at the two temperatures. Hence E may readily be calculated from the observed values of the pressure of the butadiene and the variation of surface tension with pressure at a series of temperatures. The following values are obtained from Fig. 2:—

At 50° C. $d\sigma/dp = 0.32$ dynes cm^{-2} lbs^{-1} in^2 ; at 60° C. $d\sigma/dp = 0.24$ dynes cm^{-2} lbs^{-1} in^2 ; therefore $E = 6900$ cal.

First it is of interest to note that the heat of desorption is considerably

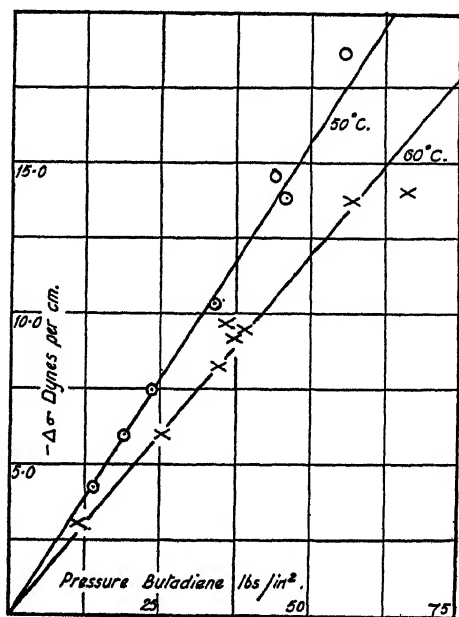


FIG. 2.—Adsorption of butadiene on hydrogen peroxide at 50° C. and 60° C.

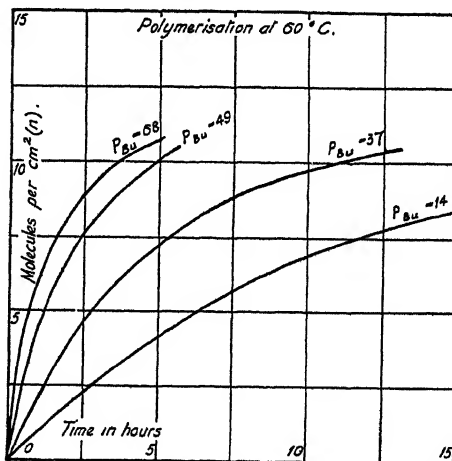


FIG. 3.—Rate of polymerisation as a function of time.

higher than the heat of vaporisation of butadiene, which is 4000 cal. This would mean that butadiene should be more strongly adsorbed on water than on butadiene whereas the reverse behaviour is observed. Secondly this figure is similar to the heat of desorption of *n*-butane, namely 7300 cal.—calculated from results at low butane pressures given by Cassel and Formstecher.¹ The presence of conjugated double bonds does not therefore appear to affect the energy of interaction of the hydrocarbon with the water surface. Again it may be noted that the heat of desorption of butane is considerably greater than the heat of evaporation—4800 cal.

Surface Properties of Polymer.

The measurements described above give only surface tensions as a function of time. To study the kinetics of the reaction we require to know how the surface concentration of polymer increases. A further experiment is therefore needed to determine the surface properties of the polymer. An immediate difficulty arises from the fact that no weighable amount of polymer is produced in the kinetic measurements, so that polymer has to be made separately by another method, and it is clear that an assumption is involved in considering the surface properties of the two polymers to be identical. With a view to minimising the probable discrepancy, attempts have been made to carry out the preparation under conditions which reproduced as closely as possible

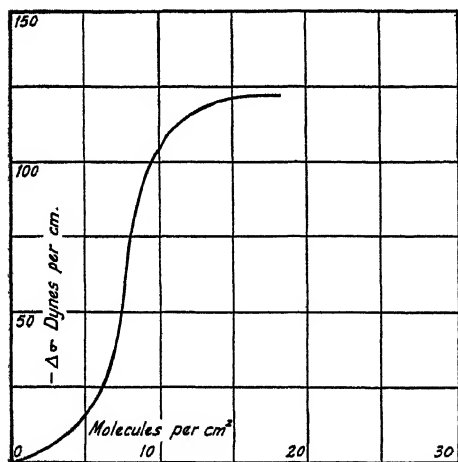


FIG. 4.—Surface pressure area curve for adsorbed polybutadiene.

those of the kinetic measurements. In the first place an apparatus was constructed in which butadiene could be bubbled slowly through a tube containing 1 volume hydrogen peroxide and thermostated at 60° C. By means of a system of valves the butadiene was passed backwards and forwards between two reservoirs which were alternately cooled in ice and salt and warmed to room temperature. The total pressure had to be kept low as the valves leaked slightly when the pressure greatly exceeded atmospheric. Under these conditions no appreciable polymerisation occurred and the experiment

was abandoned. A sample of polymer was then prepared by Imperial Chemical Industries (Dyestuffs Group), employing the following method. 100 g. of butadiene was heated with 800 c.c. of 1 volume hydrogen peroxide for 108 hours at 60° C. with shaking. A 4 % yield of a sticky polymer was obtained. This material was readily soluble in benzene, and has been employed in the subsequent experiments.

The first attempts at spreading films of the polymer were made with the Langmuir-Adam trough but in view of the fact that the surface properties were required at 60° C., this was abandoned in favour of a ring apparatus. The films were spread on 1 volume hydrogen peroxide contained in a heated pyrex dish, the edges of which had been ground flat and coated thinly with

¹ *Koll. Z.*, 1932, 61, 18.

paraffin wax. The water surface was cleaned and the film held in position in the usual way by means of barriers. These were chromium plated strips which had been coated with a monolayer of ferric stearate to prevent their being wetted. A small platinum ring was suspended from one pan of a chainomatic balance and used to measure the surface tension, the reading taken being the load required to break the ring away from the surface. The polymer was spread from benzene solution, but great difficulty was experienced in getting the films to spread. It was eventually found necessary to employ a very dilute benzene solution (about 10 mg. per litre) and to spread the film at large area, subsequently compressing to measure the surface tension lowering. Such a technique multiplies the danger of contamination of the surface and the results cannot be claimed as highly precise. They are plotted in the form of a $-\Delta\sigma \sim n$ curve in Fig. 4, n being the number of molecules of polymerised butadiene (reckoned in terms of monomer) per square centimetre of surface. As in the kinetic studies, the surface tension methods are treated as comparative only and referred to the known surface tension of water as the standard.

Calculation of the Results.

In order to find what connection there is between polymerisation rate and the variables mentioned on page 1302, it is first necessary to see what will be the most reliable measure of the velocity of the reaction.

TABLE II.—ONE VOLUME HYDROGEN PEROXIDE, 60° C.

Pressure (p) Butadiene.	14	37	49	67	69	Lbs. per sq. in.
dn/dt . . .	0.85	1.85	4.8	10	10	$\frac{\times 10^{14} \text{ mols./cm.}^2}{\text{time}}$
$(dn/dt)/p$. .	6.1	5.0	9.6	15.0	14.0	$\times 10^{-2}$
$(dn/dt)/p^2$. .	4.4	1.4	2.0	2.2	2.0	$\times 10^{-3}$

One method consists in using the surface concentration of polymer \sim time curve. For low catalyst concentrations, that is one volume hydrogen peroxide, this curve is nearly of the first order, whilst at higher concentrations up to 12 volumes the order rises slightly, to about 1.5. Hence for the 1 volume experiments the initial slope of the curve is taken as a measure of the reaction velocity. For higher concentrations it has been found more convenient to plot the results in the following manner.

At 50° C.

Pressure Butadiene.	48.5	54	Lbs. per sq. in.
dn/dt . . .	3.3	3.7	$\frac{\times 10^{14} \text{ mols./cm.}^2}{\text{time}}$
$(dn/dt)/p$. .	6.80	6.85	$\times 10^{-2}$
$(dn/dt)/p^2$. .	1.27	1.40	$\times 10^{-3}$

If the apparent order is 1.5 then

$$+ \frac{d(P_B)}{dt} = K_2 \{ (P_B)_\infty - P_B \}^{\frac{1}{2}} (C)^m (B)$$

where $d(P_B)/dt$ is the rate of formation of polymer molecules, $(P_B)_\infty$ is the final concentration of such molecules, K_2 is a constant for a given temperature and (C) and (B) are respectively the concentration of catalyst and pressure of butadiene and m an exponent. On integration this gives:—

$$K_2(C)^m(B)t = \frac{1}{(P_B)_\infty} - \frac{1}{\{(P_B)_\infty - (P_B)\}^{\frac{1}{2}}}$$

The term $\frac{1}{\{(P_B)_\infty - (P_B)\}^{\frac{1}{2}}}$ plotted as a function of time gave a straight line, the slope of which is proportional to $(C)^m(B)K_2$.

TABLE III.—75° C. — 25 LBS. PER SQ. IN. BUTADIENE.

H ₂ O ₂ (vols.)								
Concentration (C) .	1.0	2.0	2.0	5.0	7.0	9.0	12.0	
K ₂ (B) (arbitrary units)	1.1	1.8	1.9	3.3	5.3	6.2	7.2	

Tables II and III summarise the results with changing butadiene pressure and catalyst concentration respectively.

As will be seen from Table II the quantity $(dn/dt)/p$ is roughly constant up to about 50 lb. per sq. in. and thereafter rises. On the other hand

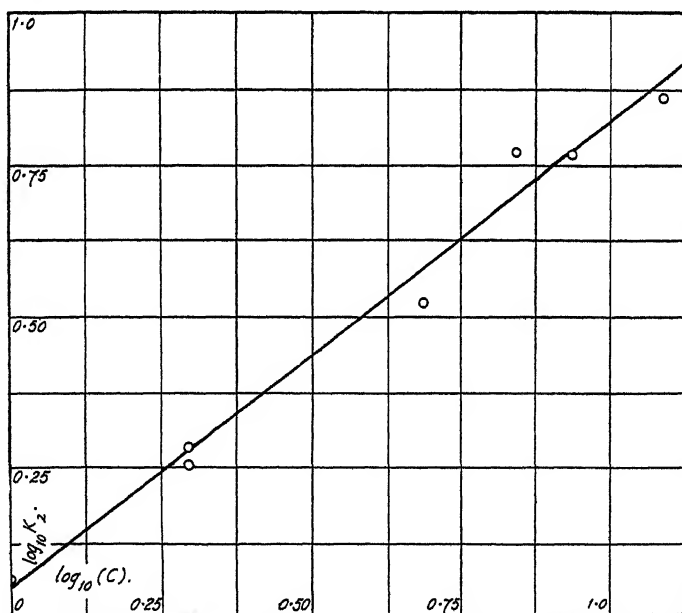


FIG. 5.—Plot of reaction velocity constant as a function of concentration of hydrogen peroxide.

$(dn/dt)/p^2$ does not show values which suggest that the reaction is second order with respect to butadiene pressure. Hence we may assume that the order with respect to butadiene pressure lies closer to unity than to the value two.

From the results in Table III, $\log K_2$ has been plotted against $\log C$ in Fig. 5. It will be observed that the straight line so obtained has a slope of approximately unity.

Experiments at 50° and 60° and 75° C. gave for the reaction an apparent energy of activation of 9000 calories. This value has, of course, to be corrected for desorption of butadiene with increasing temperature. Since the heat of desorption is 7000 cal., the apparent energy of activation of the surface reaction is $9000 + 7000 = 16,000$ cal. which is somewhat lower than that for a number of catalysed polymerisations.

Life-Time of the Active Polymer.

In carrying out kinetic investigations on polymer growth it is of prime importance to determine the life-time of the active polymer, since the type of analysis to be applied differs according to whether this life

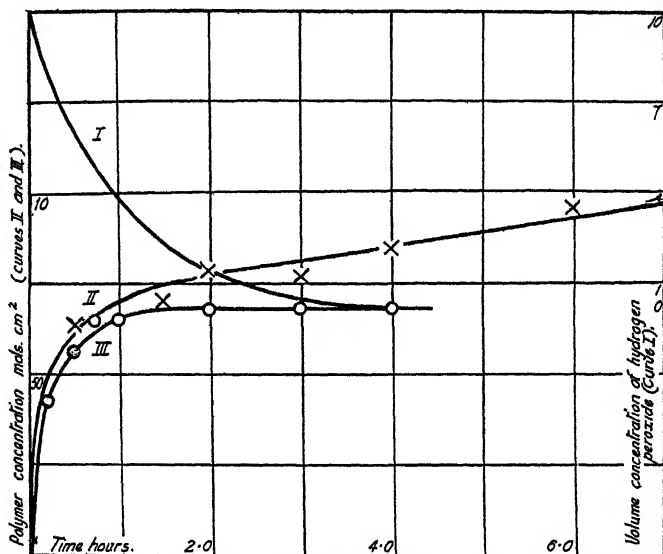


FIG. 6.—Effect of stability of hydrogen peroxide on polymerisation rate.

is short or long compared with the time of reaction. Hitherto the method of measuring this quantity has been to use the photochemical technique of starting polymerisation. In fact the only method of determining the life is by exact control of the initiation process. The method is naturally inapplicable in thermal polymerisations, but may be practicable in catalytic reactions. In the latter circumstance the difficulty to be overcome consists in obtaining control of the rate of decomposition of the catalyst without simultaneously affecting the course of the polymeric reaction itself. Fortunately this can be done with the present system by altering the pH of the hydrogen peroxide solution. It is improbable that relatively small changes in the pH value of the substrate will determine whether or not polymerisation will occur, though there may be some small change in reaction velocity. Actually, with very high acid concentrations (about 10 N.), butadiene may be polymerised but this is a different type of reaction altogether.

The experimental procedure consisted in making up two solutions of

hydrogen peroxide, one stable, with a half-life in excess of 24 hours and the other unstable with a half-life of about 0.7 hours. It may be added that the rate of decomposition of the hydrogen peroxide was not affected by the presence of butadiene. Polymerisation experiments were carried out for both samples. Fig. 6 shows the results of plotting the number of polymer molecules as a function of time. It will be seen that with the unstable catalyst polymerisation has practically ceased after one hour whereas polymerisation continued for a very much longer period with the stable catalyst. Moreover, the initial rate of the two reactions is more or less identical, which shows that p_H has not much effect on velocity. The important point, however, is that simultaneously with the decrease in polymerisation velocity with the unstable catalyst there is a corresponding diminution of the hydrogen peroxide concentration. This immediately proves that when the catalyst concentration is reduced to zero there is no continued polymerisation, as would have occurred had the life-time of the active polymer been appreciable compared with the time of reaction.

The Mechanism of the Reaction.

For convenience in discussing the mechanism of the reaction the results may be summarised as follows:—

- (a) No induction period.
- (b) Life-time of active polymer small compared with the time of reaction.
- (c) Rate of polymerisation proportional to the first power of the catalyst concentration and to the first power of the butadiene pressure.

The fact that there is no induction period shows that the rate at which the catalyst reacts with the monomer is sufficiently large to establish a stationary concentration of active molecules which start off polymerisation within an interval small compared with the reaction time. Therefore in so far as this reaction is concerned the stationary state method may be applied to calculate the concentration of the molecules formed by this primary reaction. Since the life-time of the active polymer is also short, the stationary state method may again be applied to calculate the concentration of the various active polymers present at any given time. If it is supposed that polymerisation commences when a hydrogen peroxide and a butadiene molecule react at the interface it is necessary to consider what relationship these surface concentrations will bear to the bulk concentrations in the respective phases. The solution of hydrogen peroxide in water produces little change in surface tension of the water and hence it may be supposed that the surface concentration of hydrogen peroxide is proportional to its bulk concentration. It has been shown that the surface tension lowering of the hydrogen peroxide solutions is proportional to the superincumbent pressure of butadiene. The relationship between surface concentration and pressure may readily be derived by means of the Gibbs' equation, assuming to a first approximation, that butadiene is a perfect gas and that it is insoluble in water. The number of molecules adsorbed per square centimetre Γ is given by the equation

$$\Gamma = \frac{p}{RT} \frac{d\sigma}{dp}.$$

But $d\sigma/dp$ is constant and hence Γ is proportional to p , the butadiene pressure.

Suppose that (M) and (C) respectively denote the surface concentrations of the monomer and catalyst and that k_{c_1} is the velocity constant for the interaction of these molecules to form the real catalyst, MC, for the reaction. Besides starting the actual polymerisation by interaction with another molecule of monomer at a rate $k_{p_1}(\text{MC})(\text{M})$, the MC complex may suffer two kinds of reaction. It may be dissociated again to its components, for example by collision with water molecules. Since the concentration of the water molecules in the substrate is constant, the rate of this process may be written $k_{c_2}(\text{MC})$. Secondly, collision with the monomer may result in the decomposition of the MC complex at a rate $k_3(\text{MC})(\text{M})$. In addition there is the possibility that the MC complex is broken down by the catalyst at a rate $k_4(\text{MC})(\text{C})$.

Hence

$$\frac{d(\text{MC})}{dt} = 0 = k_1(\text{M})(\text{C}) - k_{c_2}(\text{MC}) - k_{p_1}(\text{MC})(\text{M}) - k_{c_3}(\text{MC})(\text{M}) - k_4(\text{MC})(\text{C})$$

$$\text{and } (\text{MC}) = \frac{k_{c_1}(\text{M})(\text{C})}{k_{c_2} + k_{p_1}(\text{M}) + k_{c_3}(\text{M}) + k_4(\text{MC})(\text{C})}.$$

After reaction with the monomer to start polymerisation, subsequent molecules of monomer add on by a chain mechanism, that is one MC complex results in the polymerisation of a much larger number of monomer molecules. This growth is stopped eventually since the life-time of the growing polymer is finite. Again there is a choice of mechanisms, namely mutual, spontaneous or monomer destruction of the growing polymer. In the first case it can be shown that mutual termination would involve the appearance of a term containing the square root of the catalyst concentration. This mechanism therefore is excluded. The consequences of the other two types may be briefly worked out in the usual manner as follows:—

If (P_r) is the concentration of the r th active polymer and k_p and k_t represent propagation and termination coefficients then, for spontaneous termination, the relevant equations defining the concentration of such active molecules are:—

$$\frac{d(P_2)}{dt} = k_{p_1}(\text{MC})(\text{M}) - k_{p_2}(P_2)(\text{M}) - k_{t_2}(P_2) = 0$$

and in general

$$\frac{d(P_r)}{dt} = k_{p_{r-1}}(P_{r-1})(\text{M}) - k_{p_r}(P_r)(\text{M}) - k_{t_r}(P_r) = 0.$$

$$\text{Hence } k_{p_1}(\text{MC})(\text{M}) = \Sigma k_{t_r}(P_r)$$

$$\text{But } -\frac{d(\text{M})}{dt} = \Sigma k_{p_r}(P_r)(\text{M}) = \frac{k_p}{k_t}(\text{MC})(\text{M})^2 \quad . \quad . \quad (1)$$

In an exactly similar way it may be shown for termination by collision with monomer, at a general rate $k_{t_r}(P_r)(\text{M})$, that

$$k_{p_1}(\text{MC})(\text{M}) = \Sigma k_{t_r}(P_r)(\text{M})$$

$$\text{and that therefore } -\frac{d(\text{M})}{dt} = \frac{k_p}{k_t}(\text{MC})(\text{M}) \quad . \quad . \quad . \quad (2)$$

Substituting the value of (MC) in equation (1) and (2) we have

$$-\frac{d(M)}{dt} = \frac{k_{c1}(C)}{k_{c2} + k_{p1}(M) + k_{c3}(M) + k_4(C)} \times \frac{k_p(M)^3}{k_t} \quad (A)$$

and
$$-\frac{d(M)}{dt} = \frac{k_{c1}(C)}{k_{c2} + k_{p1}(M) + k_{c3}(M) + k_4(C)} \times \frac{k_p(M)^2}{k_t} \quad (B)$$

Equation (A) is certainly excluded since if k_{c2} is small compared with other terms of the denominator the polymerisation rate would be proportional to the square of the butadiene concentration. Hence equation (B) remains and the conclusion is that the polymer growth is stopped by collision with monomer. The experimental results now give a guide as to the relative magnitudes of the terms in the denominator of equation (B). First of all, $k_4(C)$ may be neglected in comparison with the remainder since $-d(M)/dt$ is proportional to the first power of the catalyst concentration. Also since $-d(M)/dt$ is proportional to the first power of (M) then k_{c2} can also be neglected. But further than this it is impossible to go, that is to determine the relative magnitudes of k_{p1} and k_{c3} . It is usually assumed that $k_{p1} \gg k_{c3}$, but there is no real justification for such an assumption. Admittedly it would be extremely difficult to devise an experiment to determine even the relative magnitudes of these quantities.

Finally, there is one point which has not been discussed. It has been shown that there is an empirical relationship between the surface tension lowering and time. This lowering has been assumed to be due to the creation of new active centres on the surface of the hydrogen peroxide and not to the progressive lengthening of the polymer chain length. The justification for this, of course, is the short life of the active polymer. The slow process really is the formation of the centre—once this is done the chain grows and stops within a very short interval. The mechanism worked out for the polymerisation shows that the chain length $\frac{-d(M)/dt}{k_{p1}(MC)(M)} = \frac{k_p}{k_t}$ is independent of (M) and (C), which in any case are maintained constant. Unfortunately these experiments do not suggest whether the polymerisation rate actually decreases during the reaction or whether it is maintained at a constant value due to the constancy of (M) and (C). The only way of deciding this question would be to measure the rate of disappearance of the butadiene. Since the area of the surface upon which polymerisation occurs is about 38 square centimetres then about 4×10^{15} molecules might be accommodated. Even if the chain length were 1000 this would only account for a pressure diminution of 6.7×10^{-4} mm. in the three litre reaction vessel. Thus no use can be made of the empirical relationship between surface tension lowering and time except that it provides an index for the rate of reaction which can be employed in addition to the initial rate of reaction.

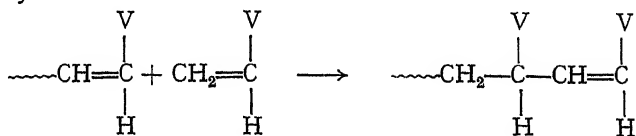
Kinetically, the conclusion about the mechanism under these conditions is that the catalyst forms with the monomer a complex which reacts further with monomer to build up a chain of butadiene molecules. The growth of this chain is stopped by interaction with monomer in a manner different from that of polymerisation.

It is not known whether addition of butadiene is 1:2 or 1:4 (it may be a mixture of both according to Hill, Lewis and Simonsen²), or

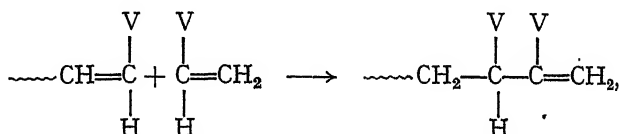
² *Trans. Faraday Soc.*, 1939, **35**, 1073.

whether the propagation of the chain involves the so-called double bond or free radical mechanisms. None the less it is possible to indicate how termination of growth might occur.

With double bond 1 : 2 addition the polymerisation may be represented by :—

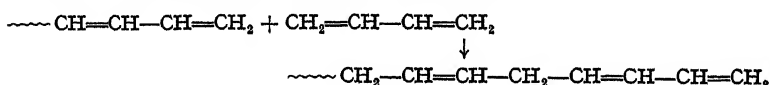


and termination by

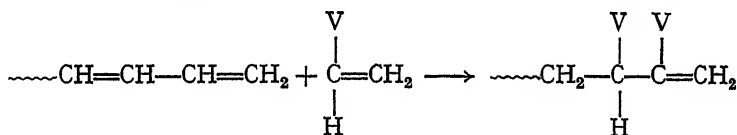


where V is a vinyl group.

In view of the symmetry of the butadiene molecule it is less easy to see how a somewhat similar process might terminate growth for 1 : 4 addition. Growth occurs by the following reaction :



and termination might occur by an occasional 1 : 2 addition thus :



to give an inactive end similar to that for 1 : 2 addition.

If the reaction is propagated by free radicals in which 1 : 2 or 1 : 4 addition occurs, it is extremely difficult to see how monomer termination could take place. Whether monomer termination in such a case might be taken as some criterion of the non-existence of free radical active polymers is an interesting question yet to be settled.

Summary.

An apparatus is described for studying the hydrogen peroxide catalysed polymerisation of butadiene at an aqueous-gas interface. The course of the polymerisation may be followed by observing the decrease of the surface tension of the solution. The reaction rate has been determined as a function of the concentration and stability of the hydrogen peroxide, the pressure of the butadiene and temperature of the system.

By varying the stability of the catalyst it is shown that the life-time of the active polymer is shorter than that of the time of reaction. By application of kinetic analysis to the experimental data it is shown that the mechanism of the reaction consists in the reaction of one catalyst with one monomeric molecule. The complex so formed starts off a polymerisation chain which is terminated by some deactivating collision of the monomer different from that for propagation.

The authors are greatly indebted to Professor E. K. Rideal for his continued interest in these experiments. One author (G. G.) is grateful to Imperial Chemical Industries Ltd. (Dyestuffs Group) for financial assistance, and the other (C. B. D.) thanks Imperial Chemical Industries Ltd. for the award of a Research Studentship which has made the work possible.

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THE EFFECT OF SALTS ON THE SURFACE TENSIONS OF GELATIN SOLUTIONS.

BY J. W. BELTON.

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The structure of the surface layer of protein solutions is of considerable interest, but it is difficult to extend to such systems the treatment which has been successfully applied to amino-acids in the previous paper. It has been found possible, however, to obtain semi-quantitative results for dilute gelatin solutions to which various salts have been added. It appears probable that at such surfaces gelatin is adsorbed together with either salt or water, depending on the nature of the salt and its concentration.

The surface tension of a solution containing gelatin is not so precise a measurement as that of a non-colloidal solution, and it appears to depend on the method of determination.¹ The variations which have been observed by different workers are probably to be explained by the non-attainment of equilibrium between the surface layer and the bulk of the solution, or by subsequent changes which occur in the surface after it has been in contact with air. The surface tension of a gelatin solution also changes with time; it is stated,² however, that it settles down to an equilibrium value after a few hours at 25° C., except for isoelectric gelatin for which it rises slowly to that of water. The surface properties and surface structure of such solutions may therefore only be deduced from experimental results which have been obtained under similar conditions and by the same method. The experiments described below are all comparable in that the same solution of gelatin and the same method were used throughout. This method depends on the formation of a new surface at the time of measurement, so that any changes in surface tension are due to changes in the bulk of the solution, or to the rapidity with which equilibrium is attained, and changes in the latter appear to be unlikely when the concentration of gelatin is kept constant. The effect of various salts at different concentrations has been investigated, and further the variations in the surface tensions of these systems over a period of several days.

¹ Johlin, *J. Biol. Chem.*, 1930, 87, 317.

² Johnston and Peard, *Biochem. J.*, 1925, 19, 281.

Experimental Method.

The surface tensions were measured by a modification of the bubble pressure method previously used by the writer.³ Dry air was passed through a finely adjusted valve, and allowed to bubble very slowly through a fine glass jet of circular cross-section of known diameter. The pressure required to blow a single bubble was measured on a butyl phthalate manometer by means of a cathetometer. In making measurements with dilute aqueous solutions it was found convenient to adjust the level of the liquid in the experimental cell by means of a pressure device so that it was just coincident with the jet, the passage of a single bubble breaking the contact. In the case of gelatin solutions, however, it was not found possible to obtain reproducible results in this way owing to the changes occurring in the surface layer. The cell was therefore modified and a platinum wire sealed into its side and then bent at right angles, so that its sharpened point was about half a centimetre above the jet. The level of the solution was adjusted by a pressure device so that it was coincident with the platinum point, as observed with the cathetometer telescope. The height between the point and the jet was constant, and was determined with the cathetometer and by calibration with water in the cell. Bubbles are thus blown at this distance below the surface of the solution, and the pressure read on the butyl phthalate manometer must be corrected by that between the point and the jet, a correction which involves the density of the solution. Accurate results could be obtained for aqueous solutions when this procedure was followed. The cell was cleaned between each solution examined with hot chromic acid, followed by washing with water and then steaming for ten minutes; it was finally dried by evacuation at 100° C. All the measurements recorded here were made at 25° C.

The gelatin was purified by repeated washing and buffering. A solution was prepared by soaking in pure water (distilled from quartz and of surface tension 72.01 dynes/cm. at 25° C.) for several hours, heating for ten minutes and allowing to cool. This solution was allowed to stand in a stoppered flask for a day and was then used as a stock solution. The various salt solutions were made from this by weight and were kept in stoppered flasks at 25° C. The salts were of Analar grade and were dried when necessary.

Surface tension measurements of each solution were taken at intervals over a number of days, and although variations over this period were noted, the values recorded were reproducible over a short period of time (1 hour). Measurements were made on the stock solution over the same period. The results are given in the accompanying table, in which m , is grams of salt per 1000 grams of water and γ is the surface tension in dynes/cm. The values of the observed manometer readings are not given, but they are of the order of 14 cm., and were measured to 0.005 cm.

Discussion.

The surface tension of the stock gelatin solution remained constant over a period of several days and then began to fall. This fall appeared to be gradual, not sudden, as it would have been had it been caused by the accidental introduction of some impurity. The surface tensions are less than that of water, indicating a positive adsorption of gelatin at the surface.

The effect of salts on the surface tension is interesting. All these salts raise the surface tension of water giving an approximately linear relation with concentration ($\Delta\gamma$ per mole of salt per 1000 gms. water is 1.7, 1.6, 1.7 and 1.0 respectively for NaCl, KCl, LiCl and KI), but when

³ Belton, *Trans. Faraday Soc.*, 1935, **31**, 1413.

gelatin is present the behaviour is different. The sodium chloride solutions show a definite maximum between 1 and 2 M., the surface tensions tending to decrease with time. In the case of potassium chloride the readings are more irregular than with any of the other salts, the first set showing very little change with concentration, with a tendency to show a maximum later. The effect of gelatin is to produce a greater lowering of surface tension as the concentration of salt increases. The addition of lithium chloride or potassium iodide produces an increase in surface tension up to a concentration of 4 M., no maximum being observed. The effect of gelatin does not increase with concentration as much as in the case of sodium and potassium chlorides; the curves, however, are not so steep as those for binary salt solutions.

In the case of some solutions a curious behaviour was observed. The pressure required to blow the first bubble was greater than the equilibrium value, to which it fell in jerks corresponding to five or six bubbles. This probably means that the unstirred solution in the neighbourhood of the jet possess a "structure" (it had stood some time to acquire the temperature of the bath), which offers a resistance to the passage of bubbles, but which is broken down by them until the surface tension of the stirred solution of gelatin is obtained. This behaviour is related to that of clay suspensions which show an increase in surface tension on standing, and has been used by the writer⁴ to examine the thixotropic properties of such systems.

Some interesting qualitative conclusions concerning the nature of the surface layer may be drawn from these data. If the Gibbs equation is combined with the Duhem-Margules' equation,⁵ we obtain

$$d\gamma = \frac{\Gamma_1}{N_1}[N_2 2RT d \ln f_2 m_2 + N_3 RT d \ln m_3] - \Gamma_3 RT d \ln m_3 \quad (1)$$

where Γ refers to the surface excess, f to the activity coefficient, N to the mole fraction and the subscripts 1, 2 and 3 to water, salt and gelatin respectively; and further, if m_3 is constant

$$d\gamma = \frac{N_2 \Gamma_1}{N_1} 2RT d \ln f_2 m_2 \quad (2)$$

If we now assume that gelatin will have only a small effect on the activity coefficient of the salt, we may find the ratio of water adsorbed on the gelatin solution to that adsorbed (${}_0\Gamma_1$) in the isomolal binary salt solution. This ratio is given by

$$\Gamma_1/{}_0\Gamma_1 = (\partial\gamma/\partial m_2)_{m_3} \Big/ \frac{d_0\gamma}{dm_2} \quad (3)$$

Thus, in the case of lithium chloride, the ratio of the slopes of the $\gamma - m_2$ curves is 10/17, and hence $\Gamma_1/{}_0\Gamma_1$ is 0.59. The adsorption of water appears to be considerably reduced, its place probably being taken by gelatin. In the case of sodium chloride the slope falls until the maximum is reached, and hence the adsorption ratio falls until it becomes zero; the adsorption of water thus becomes zero for a salt concentration between 1 and 2 M. Beyond the maximum $\partial\gamma/\partial m_2$ is negative, which means that water is removed from the surface, and that the layer then contains probably salt and gelatin. This may be

⁴ Belton, *Proc. Leeds Phil. Soc.*, 1939, 3, 565.

⁵ Cf. Belton, *Trans. Faraday Soc.*, in the press.

due to the formation of a gelatin "salt" at high salt concentrations. In the case of potassium chloride and gelatin, the first surface tension-concentration curve is almost horizontal, which means that the surface layer consists of gelatin only, and that the water layer found at the surface of the binary salt solution has been completely replaced. There may be a slight maximum, which is more pronounced in the second series, and this may be taken to indicate that there is a slight positive adsorption of salt at higher concentrations. The slopes of the $\gamma - m$ curves for lithium chloride and potassium iodide are less than for the corresponding isomolal binary salt solutions; the adsorption of water is therefore reduced, and its place probably taken by gelatin. In the case of lithium chloride, the adsorption on the salt-gelatin solution is about 70 % that on the salt solution; for potassium iodide it is about 50 %.

TABLE I.

Day.	m_2 .	γ .	Day.	m_2 .	γ .
1. Aqueous Gelatin Solutions :			(c) Lithium Chloride.		
4		66.7	18	1	68.0
13		66.7		2	68.6
14		66.7		3	69.4
16		66.5		4	70.5
18		66.4	24	1	67.5
19		65.9		2	68.3
25		65.9		3	69.1
				4	70.7
2. Aqueous Gelatin-Salt Solutions:			(d) Potassium Iodide.		
(a) Sodium Chloride.			14	1	68.5
13	1	68.5		2	68.9
	2	68.5		3	69.6
	3	68.0		4	70.0
	4	67.3	24	1	67.0
19	1	67.8		2	68.9
	2	67.7		3	69.0
	3	66.6		4	69.5
	4	65.8			
24	1	67.0	(e) Barium Chloride.		
	2	67.7	17	1.7	68.5
	3	66.5	25	1.7	68.6
	4	66.0			
(b) Potassium Chloride.					
16	1	66.8			
	2	66.3			
	3	66.4			
	4	66.3			
19	1	66.3			
	2	67.3			
	3	65.7			
	4	64.9			

Summary.

The surface tensions of dilute aqueous solutions of gelatin to which sodium chloride, potassium chloride, lithium chloride, potassium iodide or barium chloride has been added in varying concentrations, have been

measured by the bubble pressure method. The surface tension-salt concentration curve shows a maximum for sodium chloride, is almost horizontal for potassium chloride, and increases almost linearly but with a lower slope than for the isomolal salt solution, for both lithium chloride and potassium iodide. These curves are interpreted in terms of the surface structure of the solutions.

CONTRIBUTIONS TO THE GENERAL CHEMISTRY OF COLLOID-COLLOID REACTIONS. VIII.* THE MECHANISM OF PROTECTION BY SOME HIGHER CARBOHYDRATES.

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As continuation to the work already published on pure antimony sulphide sols,¹ experiments on the protection of highly purified gold and congo blue sols were carried out. Highly purified dextrin, starch (Zulowsky starch) and gum arabic sols were used as protecting colloids. The product obtained by electrodecentration (E. Dec.) of the protected gold or congo blue sols allowed more profound study of those colloid-colloid reactions.

I. Preparation and Characterisation of the Sols.

1. **Gold Sols.**—Both spark dispersed² sols and those obtained by reduction with alcohol³ were used, purified by the improved method of E. Dec.³ They were characterised by determination of the conductivity and by conductometric titration both of the sol itself and of the liquid remaining after freezing the sols. Furthermore, the Cl' concentration before (Cl₀) and after reduction (Cl_r) was determined. The data for 5 sols are given in Table I. The spark dispersed sols are called Au Z, the reduction gold sols Au A.

TABLE I.—GOLD SOLS.

Sol.							Liquid Remaining after Freezing of the Sol.					
Sol.	Au g./l.	$\kappa(10^{-5})$.	$H_{\kappa}(10^{-5} N)$.	$H_{titr.}(10^{-5} N)$.	$\kappa_{calc.}(10^{-5} N)$.	C. Eq.	$\kappa(10^{-5})$.	$H_{\kappa}(10^{-5} N)$.	$H_{titr.}(10^{-5} N)$.	Cl ₀ (10 ⁻⁵ N).	Cl _r (10 ⁻⁵ N).	Cl ₀ /Cl _r .
Au Z ₂ .	1.2	4.65	11.6	11.6	—	48	5.9	14.7	14.6	—	—	—
Au Z ₃ .	0.91	2.83	7.5	7.6	—	60	4.57	11.4	11.3	—	—	—
Au Z ₄ .	2.05	4.74	12.6	12.3	—	85	9.55	23.3	22.4	—	—	—
Au Z ₅ .	1.13	5.36	13.7	13.4	—	42	7.77	19.8	19.5	10.0	32.4	1:3.2
Au A ₂ .	1.6	6.98	17.4	15.9	8.0	33	8.8	—	19.2	16.0	45.0	1:2.9
Au A ₃ .	1.22	1.4	2.8	—	—	—	1.08	—	1.3	3.8	10.0	1:2.6
Au A ₅ .	1.14	5.35	13.4	12.5	4.6	33	—	—	—	—	—	—

* Previous publication VII, see *Trans. Faraday Soc.*, 1939, 1234. The experiments were carried out in the Institute for Medical Colloid Chemistry of the Vienna University in 1937-1938.

¹ Wo. Pauli and W. Kitaj, *Koll. Z.*, 1938, 82, 43.

² Wo. Pauli, *Naturwiss.*, 1932, 20, 551; Wo. Pauli and Ed. Russer, *Koll. Z.*, 1932, 58, 22; Wo. Pauli, Ed. Russer and E. Brunner, *Koll. Z.*, 1935, 72, 26.

³ Wo. Pauli, J. and St. Szper, *Trans. Faraday Soc.*, 1939, 35, 1178.

2. Congo Blue Sols⁴ were prepared by E.Dec. of a 0.5 % solutions of congo red. A rising voltage from 20 to 220 v. was used. The water in the outside cells was frequently changed. The E.Dec. was finished when the conductivity of the top layer remained constant. Table II gives the data for 3 congo blue sols examined.

TABLE II.—CONGO BLUE SOLS.

Sol.	(g./l.).	$\kappa(10^{-8})$.	$H_{\kappa}(10^{-8} \text{ N})$.	$M.(10^{-8})$.	C. Eq.
K ₁	1.057	3.15	6.61	1.6	24
K ₂	0.76	3.11	6.53	1.1	17
K ₃	0.425	1.21	3.8	0.65	17

3. Dextrin,⁵ **Starch**⁵ and **Gum Arabic**⁶ Sols were prepared by E.Dec. with rising voltages from 20 to 220 v. after acetic acid (final concentration 0.01 N.) had been added. Merck "Dextrinum puriss. alcoholae praec.", Merck "Zulkowsky" starch and "gum acaciae elect. albiss." were used.

TABLE III.—DEXTRIN (D), STARCH (S), AND GUM ARABIC (G.a.) SOLS.

Sol.	(g./l.).	$\kappa(10^{-8})$.	$H_{\text{titr.}}(10^{-8} \text{ N}).^*$	Ash (g./1000 g.) Dry Substance.
Dextrin	D ₂	19.4	0.13	—
	D ₄ †	46.1	0.314	1.8
	D ₈	42.3	0.398	—
Starch	S ₃	12.6	0.31	3.38
Gum arabic	G.a. ₁	49.5	1.82	44.2
	G.a. ₂	52.8	1.9	50.0
	G.a. ₃	46.6	1.64	41.7
	G.a. ₄	40.4	1.5	33.4

* $H_{\text{titr.}}$ calculated from the second break of the titration curve.

† The D₄ contains 0.027 g. of phosphorus on 100 g. of dry substance.

The data are given in Table III.

4. Purified Night Blue Sols⁴ had a concentration of 0.386 g./l. and $\kappa = 8.3 \times 10^{-6}$ mho.

II. Gold Sol + Dextrin.

An extended series of experiments on the protection of gold sols (both spark dispersed and reduction sols) by means of dextrin against KCl, BaCl₂, and La(NO₃)₃ was

carried out. Moreover, a dextrin neutralised with MgO, the excess being removed, was used. Only a short summary of this work can be given here.

Dextrin had, even in very small concentrations (to 0.001 %), a distinct protective action on the gold sols. For KCl this influence is very small, and does not vary far from the threshold value. Against bi- and tri-valent cations the protective action is much greater and the flocculation zone is much higher than the corresponding threshold value for the pure sol. The protection is never complete, even at very high dextrin content. It prevents complete coagulation, but at high salt concentration does not prevent the change of colour to blue. Analogous results were obtained with Sb₂S₃ sols,¹ in which case the sol was completely protected by gum arabic; the dextrin, however, always gave a slight turbidity. In our case the flocculation was also suppressed. Further, it was found that the

⁴ Wo. Pauli and F. Lang, *Monatshfte*, 1936, **67**, 159. Wo. Pauli and E. Weiss, *Biochem. Z.*, 1928, **203**, 104; Wo. Pauli and L. Singer, *ibid.*, 1932, **244**, 76.

⁵ Wo. Pauli, J. and St. Szper, *Koll. Z.*, 1938, **82**, 335; J. and St. Szper, *Trans. Faraday Soc.*, 1939, **35**, 667.

⁶ Wo. Pauli and L. Palmrich, *Koll. Z.*, 1937, **79**, 63; Wo. Pauli and Mrs. Hofmann-Kölbl, *unpublished*.

charging of dextrin with a bi-valent cation favours the formation of a protective dextrin shell, and so increases the protective action.

In Table IV we have given, in addition to the threshold value, the relative protection values, expressed as ratios between the threshold values of protected and pure sols.

TABLE IV.—Au Z_4 Final Concentration 50 mg./l. DEXTRIN D_4 .

Dextrin per cent \rightarrow 0.	0.	0.039.	0.26.	4.31.
KCl (10^{-2} N.)	3.3	1	5.15	5.15
BaCl ₂ (10^{-3} N.)	0.9	1	12.2	—
MgCl ₂ (10^{-3} N.)	1.5	1	19.4	—
MgCl ₂ (10^{-3} N.)	1.5	1	29.3*	48.7*

* Dextrin D_4 neutralised with MgO.

which coagulated the sol Au Z_4 (50 mg. Au/l. final concentration) when present in 8×10^{-5} N. concentration, and which at 8×10^{-6} N. gives already a marked change of coloration, the following figures for relative protection were found :

D_4 per cent.	0	0.001	0.01	0.1	1
La(NO ₃) ₃	1	10	12.5	51.2	125

III. Electrodecentration of Mixtures of Highly Purified Gold and Dextrin Sols.

Analogous to the subsequently studied case of the Sb₂S₃ sol⁸ it was found that it is possible to eliminate the excess of dextrin by E.Dec. until the top layer of the electrodialyser is dextrin-free. The dextrin remaining in the lower layer is held back by the gold sol particles. The sols Au Z_2 , Au Z_3 , Au Z_4 and Au A_3 were subjected to E.Dec. in the protected state. The sol Au Z_4 was mixed with the pure azidoid dextrin D_6 , while the others were mixed with dextrin neutralised by means of MgO.

The following example shows the progress of such an E.Dec. : 75 c.c. of Au A_3 were mixed with 25 c.c. of dextrin D_4 (the dextrin was neutralised by shaking up with MgO, the excess of which was eliminated by centrifuging), diluted to 400 c.c. and poured into the middle cell of a small electrodialyser. After 2 hours the level of the sol layer had dropped to about half the height of the electrodialyser. The top layer was syphoned off and the remaining sol replenished with conductivity water to 400 c.c. and again electrodecented. This operation was repeated until the top layer was free of dextrin. The dextrin content of the top layer was determined by drying at 110° C. to constant weight.

Each E.Dec. period was rather short ; after five successive E.Dec. the top layer was dextrin-free. The composition of the starting mixture was

TABLE V.

Electro-decentration.	$\kappa(10^{-8}$ mho) Top Layer.	Content of Dextrin of the Top Layer.
1	5.4	0.653 g.
2	4.3	0.270 "
3	3.3	0.082 "
4	3.4	0.005 "
5	2.0	0.000 "
		1.010 "
		Initially added 1.074 "

⁷ H. Freundlich and E. Loening, *Koll. Beih.*, 1922, 16, 1.

⁸ Wo. Pauli and H. Zentner, *Trans. Faraday Soc.*, 1939, 35, 1234.

0.915 g. Au/l. and 11.5 g. D₄/l., corresponding to a 12-fold excess of dextrin. In the purified final product the gold content was 1.677 g./l. and the dextrin concentration was 0.06 g./l. The proportion of dextrin to gold was therefore only 1/28, *i.e.*, only 0.3 % of the dextrin initially added was fixed by the gold particles. All these splendidly red sols can be electrodeposited at 220 and more volts without any particular precautions, *e.g.*, the use of a collecting vessel, being taken.

In Table VI the data for two spark dispersed sols as well as one reduction sol Au A₃ are given. The differences between these and the pure unprotected initial sols can readily be seen. In the case of the sol Au A₃ which originally had as Gegenions not only H⁺ but also a preponderance of K⁺ ions, an exchange of H⁺ against K⁺ has taken place. The conductivity of the sol underwent an increase and the values for H_κ and H_{titr} coincided.† The other sols show, referred to the same Au content, a decrease in conductivity to about a half or less compared with the initial ones. The ratio D/Au varied between 0.15 to 0.04 in the case of all 5 sols, and seemed to be independent of whether the dextrin was acidoid or one neutralised with MgO. For Au Z₄ which was mixed with the acidoid dextrin, the ratio D/Au was 0.13, which is the amount of dextrin for 1 g. Au/l.

TABLE VI.—GOLD SOLS + DEXTRIN.

Sol.	Initial Sols.			"Protected" Sols.*							
	Au (g./l.).	$\kappa(10^{-5})$.	$\kappa(10^{-5})$ (per 1 g./l.).	Au (g./l.).	D (g./l.).	MgO (g./l.).	$\kappa(10^{-5})$.	$\kappa(10^{-5})$ (per 1 g./l.).	H _{titr.} (10 ⁻⁴ N).	H _κ (10 ⁻⁴ N).	C. Eq.
Au Z ₃ (a)	0.91	2.83	3.1	0.382	0.032	0.03	0.45	1.25	0.10	0.11	172
Au Z ₃ (b)				0.37	0.035	0.02	0.52	1.40	0.12	0.12	155
Au A ₃	1.22	1.4	1.15	1.677	0.06	0.02	6.0	3.57	1.5	1.5	63
Au Z ₄	2.05	4.72	2.30	2.82	0.37	—	3.26	1.16	0.834	0.815	169

* The sols obtained by E.Dec. of a mixture of hydrophobic and hydrophilic colloids will be called "protected" sols.

To two portions of Au Z₃ dextrin was added. In one case a quantity just sufficient to protect the gold sol, in the second a quantity 10 times as large. In both final protected sols we found the ratio D/Au of 0.09 in good agreement with the above value.

Electrochemical analysis of the behaviour of our purified protected sols shows that the surfaces of the particles have preserved their character of a gold sol. This is shown by the presence of ionogenic groups of the same type as in the original colloid. The amount of H⁺ ions given to the ionic atmosphere by the protective colloid was insignificant, even in the case of the acidoid dextrin.

On the other hand, comparison of initial and purified protected sols shows that the charge density was decreased by one half. There is no ground for assuming that removal of the inogenic groups to the top layer takes place during the E.Dec. We must, therefore, admit that the surface of the gold particles was partially covered (say a half or a little

† We did not interpret more closely the results for these sols because of the uncertainty in the original colloid equivalent which was due to both H and K Gegenions.

more) by a dextrin shell. This assumption has already been justified in the case of Sb_2S_3 sols.⁸ It is difficult to say whether this shell is in the form of a porous film or a mesh-like net. The linear shape of the dextrin particles speaks for the latter.

The ionogenic groups are capable also of dissociation, as they can be inactivated and discharged by increase of the concentration of the Gegenions. The penetrability of the dextrin film increases with the concentration of the coagulating ions. The relative protection increases with the valency of the cations. Table VII refers to such purified protected gold.

TABLE VII.

GOLD SOL Au Z_4 Final Concentration 50 mg. per Litre.
DEXTRIN D_6 " " " " " "

KCl.

Normality. Sol.	$4 \cdot 10^{-1}$	$2 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	$4 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
Au Z_4	+++	+++	+++	+++	I	—	—	—	—
Au $\text{Z}_4 + \text{D}_6$	+++	+++	+++	+++	—	—	—	—	—

 BaCl_2 .

Normality. Sol.	$4 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Au Z_4	+++	+++	+++	+++	+++	+++	III	I	—
Au $\text{Z}_4 + \text{D}_6$	+++	+++	++	II	I—	—	—	—	—

 $\text{La}(\text{NO}_3)_3$.

Normality. Sol.	$8 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-5}$
Au Z_4	+++	+++	+++	+++	+++	+++	+++	+++	III
Au $\text{Z}_4 + \text{D}_6$	+++	+++	II	II	II	I	—	—	—

Notation used :—

- | | |
|----------------------------|---------------------------------|
| +++ Complete flocculation. | II Violet-red. |
| ++ Partial flocculation. | I Slight change of colour. |
| + Slight flocculation. | I— Very faint change of colour. |
| III Blue coloration. | — Sol not affected. |

* The liquid over the precipitate was pink.

It is seen that the "protected" sols, in which the dextrin excess was removed by E.Dec., are not protected against electrolytes in sufficiently high concentrations. Complete coagulation took place. This does not occur, however, when very high dextrin concentrations, e.g., 10 % were used (without subsequent E.Dec.). In this case a blue coloration appears, but no coagulation. The blue coloration is due to the approach of primary and the formation of secondary particles. The aggregation of these and complete coagulation is hindered by the dextrin shell. It must also be assumed in this case that a stronger dextrin shell is present, which is partially reversible: at smaller dextrin concentrations it becomes weaker. This was confirmed by the simultaneous E.Dec. experiments.

Though the "protected" sols were coagulated by electrolytes, they were, however, properly protected against some forms of autocagulation. Thus, for instance, it was very difficult to produce coagulation by freezing. The inactivation of the atmosphere of their own Gegenions which follows the increase of concentration during the freezing of the solvent merely produces a change of colour to blue. This indicates a certain degree of mutual approach of the primary particles. Irreversible coagulation of the particles is prevented by the dextrin shell, and when the frozen sol was melted up again it once more became red. Not less than 12 repeated freezings were needed to get a flocculation of the sol and a clear top layer. If the top layer and the coagulate were left in contact for a few days, the top layer became blue and, later on, even reddish. A major part of the coagulate, however, does not go into solution at all.

Further, the "protected" sols were not sensitive to high voltages during the electrodecentration. While an ordinary gold sol in a simple electrodialyser coagulated when a voltage higher than 5.6 v. was applied, the protected sols stand up to 220 and even 440 without undergoing any visible change.

IV. Gold Sols and Gum Arabic.

The highly purified gum arabic sol, although it has the same sign of charge, has a pronounced protecting effect on gold sols. It completely protects the reduction gold sols, when present in a final concentration of 0.001 %, against KCl, BaCl_2 and $\text{La}(\text{NO}_3)_3$. The spark dispersed sols are protected by 0.01 % of gum arabic final concentration. A blue coloration appears in the sols at high concentrations of electrolytes, as will be explained below. In general, we have confirmed the results of Pauli, Russer and Schneider.⁹

In some cases the addition of gum arabic gave a violet-blue tinge to the gold sols. We observed this effect with G.a.₂, G.a.₃, and G.a.₄, but not with G.a.₁. This effect is increased in presence of electrolytes, even in quantities below the threshold value. Pauli and colleagues,⁹ who found a similar effect, explained it by the fact that gum arabic on standing gives decomposition products, which partially reduce the gold sols. As a matter of fact, the reducing monoses (e.g. dextrose) or bioses (e.g. lactose) give a similar blue coloration in the gold sols which is strengthened by electrolyte addition (KCl in 4×10^{-3} N. final concentration).

Reduction gold sols are partially flocculated by addition of acidoid gum arabic alone. The optimum concentration of gum arabic is, in this case, 0.25 % final concentration. Below 0.1 % and above 1 % the flocculating effect disappeared. A concentration of 0.5 % gives a change of colour only. We have not found such flocculation when gum arabic was neutralised before being added. The spark dispersed sols do not give similar effects. We, therefore, assume that the flocculation is due to H ions from the gum arabic. At low gum arabic content the concentration of H^+ was too small, at high contents the gum arabic has protected the gold sol particles against its own H ions. We have, in fact, found different threshold values against H^+ for the reduction and spark dispersed sols (Table VIII).

It is seen that the threshold value for the reduction gel sols is about one-third of that for the spark dispersed sols. On the other hand, potentiometric measurement with a glass electrode showed that the H^+ activity (a_{H}) of a 0.25 % solution of gum arabic is about 5.6×10^{-4} N. which is near to the threshold value of the reduction gold sols. The structure of the spark dispersed and reduction sols being analogous, the difference in their behaviour against H ions may lie in the degree of dispersion.

⁹ Wo. Pauli, Ed. Russer and G. Schneider, *Biochem. Z.*, 1934, **269**, 158.

TABLE VIII.—Final Concentration of Gold Sols: 50 mg./l.

HCl.

Normality. Sol.	$1 \cdot 10^{-2}$	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$4 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
Au Z_4 .	+++	+++	++	II	I	—	—	—	—
Au A_5 .	+++	+++	+++	+++	III	II	I	—	—

The electrodecantation of a mixture of gold and gum arabic sols gives results which explain the difference in the protective power of dextrin and gum arabic. While the gum arabic sols cannot very well be electrodecanted, on account of their high viscosity and hydration, the addition of gold sol makes the E.Dec. easy. The level of the mixture of gold and gum arabic sols dropped to half the height of the electrolyser in about 2 hours. The potential applied was 220 v. at a distance of 10 cm. between the electrodes.

Table IX gives the data for the "protected" Au Z_4 sol; 50 c.c. of this sol were mixed with 10 c.c. of G.a.₂ diluted to 400 c.c. and submitted to electrodecantation until the top layer was gum arabic free. The presence of gum arabic was detected by evaporation to dryness of the top layer, or by decomposition with HCl and determination of the resulting monoses with Fehlings' solution.

TABLE IX.—50 c.c. OF AU Z_4 + 10 c.c. G.A.₂; AFTER ELECTRODECANTATION.

Au. g./l.	G.a. g./l.	$\kappa(10^{-6})$. Top Layer.	$\kappa(10^{-4})$. Sol.	$a_H(10^{-3} \text{ N.})^*$	$c_H(10^{-3} \text{ N.})^\dagger$	$c_H(10^{-3} \text{ N.})$. Calc. from G.a. Content.
1.85	4.6	4.0	2.78	1.0	4.02	4.2

* Glass electrode.

† Second break of the titration curve.

In the original mixture the ratio G.a./Au was 5/1. The same ratio in the protected sol after E.Dec. is 2.5/1. In the case of dextrin we had respectively a ratio of 12/1 in the mixture, the dextrin amount being reduced finally to 3/1000.

The H^+ titration curve of the protected sol is analogous to that of the pure gum arabic sol. The curve has two breaks, the second of which shows the total H^+ concentration, corresponding to the gum arabic content. The concentration of H ions of the gold sol particles ($1.05 \times 10^{-4} \text{ N.}$) is negligible by comparison. Further experiments indicate that a complete covering of the gold particles took place and that their Gegenions had been inactivated. An experiment with two portions of the gold sol-gum arabic mixture in different proportions and subjected to a severe E.Dec. repeated 10 times with 220 v. gave similar results. During the E.Dec. the gum arabic become more concentrated. No quantitative interpretation of the results is possible, owing to the simultaneous electro-decantation of free gum arabic, which was not the case with dextrin. The protective power, as shown in Table X is complete, contrary to that of dextrin.

The simple mixtures of gold and gum arabic sols at the same electrolyte concentrations show a blue coloration. Sols subsequently subjected to E.Dec. do not change their colour, because the formation of a protecting shell necessitates a certain time. When electrolyte is added to the gold sol, together with, or only a short time after, the gum arabic, the shell may be only incompletely formed and coagulation may take place. Since, after the rapid coagulation, the number of particles and, thereby, the

probability of their collision decreases, the formation of a protective shell may proceed and stop the coagulation.^{10, 11} When, after addition of protective colloid, the mixture is subjected to E.Dec., the conditions are favourable for free formation of a protective shell and, therefore, a fully protected sol is obtained.

The gold-gum arabic sols were stable not only against high voltage during the E.Dec., but also against coagulation by freezing. The stability

TABLE X.—Au Z₄ + G.A.₂.

KCl.

Normality.	I	4·10 ⁻¹	2·10 ⁻¹	1·10 ⁻¹	4·10 ⁻²	2·10 ⁻²	1·10 ⁻²	4·10 ⁻³	2·10 ⁻³
Sol.									
Au Z ₄	+++	+++	+++	+++	+++	I	—	—	—
Au Z ₄ + G.a. 0.01 %*	III	III	II	II	I—	I—	I—	I—	I—
Au Z ₄ + G.a. 0.012 %†	—	—	—	—	—	—	—	—	—

BaCl₂.

Normality.	4·10 ⁻²	2·10 ⁻²	1·10 ⁻²	4·10 ⁻³	2·10 ⁻³	1·10 ⁻³	4·10 ⁻⁴	2·10 ⁻⁴	1·10 ⁻⁴
Sol.									
Au Z ₄	+++	+++	+++	+++	+++	+++	++	III	I
Au Z ₄ + G.a. 0.01 %*	II	II	II	II	I—	—	—	—	—
Au Z ₄ + G.a. 0.012 %†	—	—	—	—	—	—	—	—	—

La(NO₃)₃.

Normality.	4·10 ⁻³	1·10 ⁻³	8·10 ⁻⁴	4·10 ⁻⁴	2·10 ⁻⁴	1·10 ⁻⁴	8·10 ⁻⁵	4·10 ⁻⁵	2·10 ⁻⁵	1·10 ⁻⁵	8·10 ⁻⁶
Sol.											
Au Z ₄	+++	+++	+++	+++	+++	+++	+++	+++	++	III	III
Au Z ₄ + G.a. 0.01 %*	III	II	II	I	I	I—	I—	I—	I—	I—	I—
Au Z ₄ + G.a. 0.012 %†	—	—	—	—	—	—	—	—	—	—	—

* Mixture.

† " Protected " sols.

against freezing is even higher than in the case of gold-dextrin sols, which became blue when frozen, because the thin layer of dextrin permits a sufficient approach of the primary particles to cause a change of colour. The gold-gum arabic particles, however, have a more complete covering, which exhibits all the proprieties of gum arabic, and the protective effect is complete against any sort of coagulation.

Gold sols + starch. The purified soluble Zulkowsky starch gives results similar to dextrin.

V. Congo Blue Sols + Dextrin.

We failed to find, even in high acidoid or neutralised dextrin concentrations (10 %) any protective effect against KCl, BaCl₂, or La(NO₃)₃.

¹⁰ A. v. Buzágh, *Koll. Beih.*, 1930, **32**, 136.¹¹ H. Freundlich, *Kapillarchemie*, Leipzig, 1932, p. 455.

The action of KCl was examined up to 1 N. final concentration, the BaCl_2 to 4×10^{-2} N. (threshold value 2×10^{-3} N.) and that of $\text{La}(\text{NO}_3)_3$ to 4×10^{-3} N. (threshold value 8×10^{-5} N.). Similarly, no protection with the Zulkowsky soluble starch was found. (The concentration of congo blue, as used in the flocculation tubes was 3.15×10^{-3} %.)

We did find, however, an apparent sensitisation effect, which increased with rising dextrin concentration. Flocculation was observed for KCl at 2×10^{-1} to 2×10^{-2} N., for BaCl_2 from 1×10^{-3} to 4×10^{-4} N. and for $\text{La}(\text{NO}_3)_3$ from 4 to 2×10^{-5} N. The dextrin concentration was varied from 0.5 to 10 %.

The true sensitisation effect is, according to one of us (W. P.), caused by a nuclear aggregation of hydrophobic on the hydrophilic particles present in low concentrations. In our case we have a different effect, the sensitisation increasing with dextrin concentration even to a fairly high dextrin content (10 %). At such a high dextrin concentration it is difficult to visualise an aggregation of gold particles on a few dextrin particles; the apparent sensitisation effect is probably caused by H ions. The Congo Blue sol is particularly sensitive to traces of acid, *e.g.* contained in the laboratory air. This is, as mentioned by Pauli and Singer,⁴ due to the transition of the imino to imonium groups, which give a more zwitterionic character to the dye molecules. The H ions needed for such a sensitisation were provided by the hydrophilic sol. They are driven out of the hydrophilic particles, according to the law of mass action, by the neutral salts added. The bi- and tri-valent ions produce this phenomenon even in lower concentrations. This explanation accords with the analytical results. The hydrophilic sols, on the other hand, have been proved to be free of decomposition products such as lactic acid.

The same apparent sensitisation was found at corresponding electrolyte and hydrophilic colloid concentration, for the mixture of Congo Blue and gum arabic sols. The lack of any association between Congo Blue and dextrin, starch or gum arabic particles is confirmed by the absence of any region of protective action, which is consonant with the true sensitisation effect.

The Electrodecentration of Congo Blue + Dextrin. 60 c.c. of Congo Blue K_1 was mixed with 10 c.c. of dextrin D_0 , diluted to 400 c.c. and subjected eight times to E.Dec. A potential of 220 v. was applied each time and the sol layer allowed to drop to one-quarter of the height of the electrodialyser. After eight E.Dec., performed very rapidly, the top layer was found to be dextrin free. The sol obtained was not protected at all, and contained no dextrin.

VI. Congo Blue + Gum Arabic.

The acidoid gum arabic does not protect Congo Blue against KCl. Gum arabic neutralised with MgO, however, as already shown by Pauli, Russner and Schneider,⁹ protects the Congo Blue sol completely. In the latter case a bridge formation between the uronic and sulphonic acid groups by means of the Mg is possible, so that the Congo Blue sol particles become covered by a shell of gum arabic. The protection of Congo Blue sol by medium concentrations of acidoid gum arabic against bi- and tri-valent cations can be similarly effected.

There is, however, a difference between the two cases. The MgO also neutralises the H ions of the acidoid gum arabic, while if Ba^{++} or La^{+++} are added in the form of neutral salts, they can only displace the H ions when they are present in higher concentrations. When the concentration of gum arabic also is high (over 1 %) the concentration of the displaced H ions may become so great that coagulation of the Congo Blue may occur.

We see, therefore (Table XI) that the protective action at high salt concentrations passes through a maximum as the concentration of gum arabic is increased.

TABLE XI.—CONGO BLUE, FINAL CONCENTRATION $3.15 \times 10^{-3} \%$ + G.a.₂.
N La(NO₃)₃.

G.a. ₂ %.	0	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$4 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
— . .	—	+++	+++	+++	+++	+++	+++	—	—
10 . .	—	+++	+++	++	+	+	—	+	+
1 . .	—	—	—	—	—	—	—	—	—
0.1 . .	—	+++	+++	+	—	—	—	—	—
0.01 . .	—	+++	+++	+	—	—	—	—	—
0.001 . .	—	+++	+++	+++	+++	—	—	—	—
0.001 . .	—	+++	+++	+++	+++	+++	+	—	—

As expected, the E.Dec. of a mixture of Congo Blue and pure gum arabic sols yields a sol which is not noticeably protected against KCl.

Purified electro-positive Night Blue, as already pointed out by Pauli, Russer and Schneider, gives, when gum arabic is added to it in equivalent proportions (charge-equivalence) a colloid-colloid flocculation. There is, moreover, a narrow region (between 1×10^{-4} and $1 \times 10^{-5} \%$ final gum arabic concentration) where a true nuclear sensitisation, in other words an aggregation of hydrophobic on hydrophilic particles takes place. At higher gum arabic concentrations (0.01 to 0.1 %) we found a considerable protection against KCl. The dextrin (D₄), however, which lacks a polyvalent character, gave no sensitising, protective or coagulating region. Only against low concentrations of KCl (4×10^{-2} N.; threshold value 4×10^{-3} N.) was a protective action observed, explainable by the formation of a protective layer through aggregation of negative dextrin with the Night Blue particles.

VII. Review of Results.

Electronegative Congo Blue sols are not protected by dextrin or gum arabic sols. Gold sols which have the same sign of electrical charge are, however, protected by both these hydrophilic sols, in analogy with Sb₂S₃ sols which we have closely investigated.⁸

According to one of us (W. P.), the colloid-colloid reaction is based on the interaction of the definite surface groups of the one colloid with those of the other. On this assumption, the case of oppositely charged sols, bearing in mind a possible polarisation of the charge, is relatively simple. It is essentially an interionic reciprocal action, as, *e.g.*, in the reaction of gum arabic with the positive Night Blue or iron oxide sols. The reaction between two negative colloids requires some other explanation.

Pauli and Kitaj¹ indicated the likelihood that the metallic ions of the wholly hetero-polar surface of Sb₂S₃ sol particles react with the alcoholic groups of the monoses in the carbohydrates. In the modern sense, this would involve interaction between a central metallic ion and dipolic groups in the first Werner co-ordination sphere. The charging ionogenic groups, so far as they are ionically active, cannot be said to favour the formation of the protective shell. It is remarkable that colloidal gold (much of the particle surface of which appears not to be

heteropolar but purely metallic) behaves like Sb_2S_3 sol. We must, therefore, consider not only a reaction between the monose residues and the inactivated superficial complexes, but also some relations of these residues to the elementary gold surface. In the case of Congo Blue as the hydrophobic negative colloid, there is no reason to assume such a reaction within the first co-ordination sphere of the metallic ions.

The analogy between the dextrin shell and true co-ordination compounds of such a type as tri-glycol-cobalt chloride¹² should not be extended too far. It exists in so far as the attraction forces between the alcoholic dipoles and a central atom are concerned. The alcoholic groups may fill the first co-ordination sphere and be firmly held there, such is as in the case of dihydrate of the above-mentioned cobalt complexes, in which the water dipoles are forced into a looser combination in the second sphere. Steric consideration of the monose link chains of our carbohydrates preclude such a complete co-ordination. The conception of adhesion on a pure metallic surface is in some respects similar to that on a heteropolar metallic surface. It is not inconsistent with the idea of a metal lattice consisting of positive atomic residues embedded in an electronic medium.

As expected, we find a quantitative difference in the amount of dextrin held by the particles of Au sols and Sb_2S_3 sols. The latter, with its entirely heteropolar surface, take up a multiple of the quantity of the former.

Pauli and Zentner⁸ found that the surfaces of particles of protected Sb_2S_3 sols preserve the electro-chemical character of Sb_2S_3 sol, but they differ in so far that the ionisation of their ionogenic groups is reduced to about a half the original value. The E.Dec. of a gold-dextrin mixture gave us similar results, indicating that in both cases the particle surface is covered by a mesh-like, coarsely porous film of dextrin. The film gives only partial protection against flocculation with electrolytes. It is, however, sufficient to hinder electro-deposition during E.Dec. at high voltages and, to a large extent, to suppress irreversible coagulation by freezing.

The protective effect against uni-valent ions cannot be explained in the case of the Au + D sols by a simple dilution effect, reducing the total charge (Burton rule). This requires an increase of the threshold value of uni-valent ions, but, on the other hand, a decrease of that of poly-valent ions, with dilution; we found, however, an increase in both cases. We must assume that the access of the coagulating ions is prevented by the dextrin film. This effect can be overcome more easily at higher diffusion potentials.

Gum arabic renders the Au and Sb_2S_3 sols immune to electrolytes and freezing to a much larger extent. There is a very compact and strong gum arabic shell. The surface of the particles exhibits a purely gum arabic behaviour.

In this connection despite the somewhat different mechanism of reaction, similar observations have been made on collodion particles and gelatin,¹³ on paraffin emulsions and gelatin,¹⁴ and, in particular, on quartz particles with albumen and gelatin¹⁵ at different pH . In the latter case

¹² A. Grün and E. Boedecker, *Ber.*, 1910, 43, 1051.

¹³ J. Loeb, *J. gen. Physiol.*, 1923, 5, 395, 479, 505.

¹⁴ D. Limburg, *Rec. Trav. Chim.*, 1926, 45, 875.

¹⁵ H. Freundlich and H. A. Abramson, *Z. physik. Chem.*, 1928, 133, 51; H. A. Abramson, *J. Am. Chem. Soc.*, 1928, 50, 390.

there is the same dependence between pH and electrokinetic velocity as with pure albumen. Experiments with unpurified gold-gelatin mixtures¹⁶ also show the dependence between pH and the velocity of electrophoresis.

Congo Blue can only be protected with gum arabic if this latter has previously been allowed to take up polyvalent ions such as Ba, Mg or La which form a bridge between the charging sulphonic groups of the Congo Blue and the uronic acid groups of the gum arabic.

The effect of secondary liberation of H ions from the gum arabic by addition of neutral salts has already been discussed.

If we assume that the mechanism of protection of the metallic sols is basically the same for gum arabic and dextrin, we still have to explain the quantitative difference in their protective power. Possibly it lies in the large difference of size and shape of their respective particles. The dextrin particle has a molecular weight of about 6000 and a linear shape, which favours the idea of net formation. Gum arabic has a molecular weight of about 250,000,¹⁷ and is probably present as spherical clusters with interlaced branching chains⁶ (large stickiness, no tendency to gel formation). This type of structure seems to be more favourable for the formation of a stronger and more compact shell.

We have emphasised, in this and in previous papers, the rôle played by the surface groups of the particles in colloid-colloid reactions. The electro-chemical and structural conception of their reciprocal action is of importance for the elucidation and classification of the protective effect.

The interionic forces are responsible for the reaction of oppositely charged colloids. One of them must be hydrophilic, and, if present in excess, it can protect against flocculation with electrolytes. In the case of proteins, which are typical hydrophilic zwitterions, the formation of a protective shell on hydrophobic particles of both signs is caused similarly by an interionic, reciprocal action. Here, however, we must have a further mechanism, *e.g.*, the effect of adding a neutral salt to prevent a denaturation of the protein shell¹⁸ and to produce a protective effect.

Finally we have an interesting variation of the interionic action, when polyvalent cations form bridges between the ionogenic complexes of two similarly charged hydrophobic and hydrophilic colloids and thus produce a protective shell.

Our observations and those on Sb_2S_3 sols have shown a further protective mechanism. The protective film is, in this case, formed by virtue of attractive forces between the dipole groups of the hydrophilic colloid and the metallic atoms, especially metallic ions, of the hydrophobic colloid. The protective shell may be more or less complete according to the structure of the hydrophilic colloid.

We have grouped the protective effects according to their mechanism. It is obvious that there is a wide field still open. The principles which we have applied to our work on highly purified sols should be equally useful in investigations of related problems.

One of us (J. S.) is indebted to the Feliks Wislicki Foundation, Warsaw, for a grant for foreign research.

¹⁶ W. Reinders and W. M. Bendien, *Rec. Trav. chim.*, 1928, **47**, 977.

¹⁷ H. B. Oakley, *Trans. Faraday Soc.*, 1935, **31**, 136; F. G. Donnan, *J. Chem. Soc.*, 1939, 713.

¹⁸ W. Pauli, *C.r.Lab. Carlsberg. Ser. chim.*, 1938, **22**, 416, *Sörensen Jubilee*.

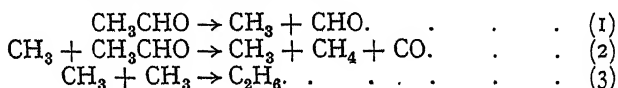
THE DECOMPOSITION OF ACETALDEHYDE AND DEUTERO-ACETALDEHYDE.

By R. E. SMITH.

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Introduction.

To explain the thermal decomposition of acetaldehyde two theories have arisen. F. O. Rice on the one hand (*J.A.C.S.*, 1934, **56**, 284) and Letort on the other (*J. Chim. Phys.*, 1937, **34**, 355) have developed the theory of a radical mechanism as follows:



In regard to pressure variation this theory would lead to a $3/2$ order reaction. It would also predict (1) inhibition by radical absorbing gases, and (2) stimulation of those reactions whose propagation depends on free radicals of a similar nature. As an example of the first, one would expect ethylene to produce an inhibitory effect on a radical reaction. Fletcher and Rollefson¹ found that a purely radical decomposition could be initiated by the addition of ethylene oxide. They have shown also that this induced reaction is subject to inhibition by ethylene, being reducible to one-third by moderate proportions of ethylene. An example of (2) might be found in ethane. Around 600° C. this decomposes by a thermally initiated chain reaction propagated by radicals.² At 50° lower it seems likely that the presence of similar radicals from the acetaldehyde would stimulate an acetaldehyde-ethane mixture to a faster pressure increase which would proceed beyond the normal end-point.

However, evidence has been put forward³ to show the reaction to be kinetically composite, consisting of several virtually independent decompositions. These differ among themselves both in the mode of activation and in the mean time lag between activation and the split up of the molecule. Because of this latter assumption we see that the predominance of a particular mechanism will vary with pressure. The ones of longest time lag are more important at lower pressures, but, as the pressure is increased they reach a limiting rate and become of the first order. On the other hand, a mechanism which activates a molecule with a greater probability of decomposition will remain of the second order over a higher range of pressures. This gives rise to a pressure-rate curve of the characteristic segmented shape as was found in the experiments of Fletcher and Hinshelwood. From this one might expect a gradual change in the properties of the reaction on moving from one pressure range to another since the proportions of the different mechanisms will shift.

¹ *J.A.C.S.*, 1936, **58**, 2135.

² Staveley, *J.C.S.*, 1937, 1568.

³ Fletcher and Hinshelwood, *Proc. Roy. Soc., A*, 1933, **141**, 41.

This latter theory makes no assumptions concerning the position of the critical bond in the molecule. So either the carbon-carbon or the carbon-hydrogen bond activation may be the method by which the reaction proceeds. Presumably the complete ejection of a methyl group or hydrogen atom will lead to a chain reaction so that the most likely internal rearrangement would be the direct migration of the hydrogen atom from the aldehydic group to the methyl group. The effect of deuterium substitution might throw light on this last problem. For this change would be of small consequence to the carbon-carbon link but productive of a marked and characteristic influence on the carbon-hydrogen link. In the chain reaction given above the observed activation energy will be given by

$$E = E_2 + \frac{1}{2}E_1 - \frac{1}{2}E_3$$

where E_1 , E_2 and E_3 are the activation energies of the reactions (1), (2) and (3) respectively. The only one of these likely to be much changed by the substitution of deuterium for hydrogen is E_2 , which, according to the chain scheme amounts to about 20 % only of the total E . The greatest term is the $\frac{1}{2}E_1$, which is chiefly concerned with the breaking of the carbon-carbon bond. On the other hand in the direct rearrangement the activation of the carbon-hydrogen bond may constitute the major part of the observed E .

With these possibilities in mind, the reactions of acetaldehyde and the completely substituted deuterio-acetaldehyde were compared, and the specific effect of several gases studied.

Experimental.

The methods used in the experiments were similar to the ones described in previous papers from this laboratory. The gas reacted in a silica bulb of about 200 c.c. volume contained in an electric furnace, the reaction being followed manometrically. The "dead space" amounted to about 2 % of the total volume. The temperature was measured by means of a platinum-platinum-rhodium thermocouple, checked daily by standard runs or later by the use of a standard potentiometer. It was constant to within half of a degree.

The acetaldehyde was carefully fractionated from the purest that could be obtained. It was then stored in a bulb attached to the apparatus and all air, known greatly to accelerate the reaction, was removed by freezing the acetaldehyde in liquid air and evacuating for several minutes; after this it was distilled over a second bulb. The deuterio-acetaldehyde (99.5 %) was obtained from the Norsk Hydro Co., and fractionated inside the apparatus. In experiments with other gases the mixture was made in a premixing vessel and rendered homogeneous before introduction into the furnace.

With both the light and the heavy acetaldehyde the pressure was found very nearly to double on decomposition. Numerically the average end-point corresponded to about a 97 % increase over the initial pressure, the tendency being towards lower end-points at higher pressures. This could easily arise from the effect of the dead space or slight polymerisation. In all cases the light and heavy compounds gave similar results.

To determine the rate of a particular run three quantities were determined, first the initial rate, taken from the tangent at zero time to the pressure-time curve; secondly the reciprocal of the time for the pressure to increase 50 % of the initial pressure; and thirdly the reciprocal of the time for the pressure increase equal to $\frac{1}{2}$ of that corresponding to the actual end-point. These last two differ by only a correction term. The

comparison was made in these different ways to eliminate errors due to slight variation in end-point, and to show that the trend in the ratio given in Table II was not a function of uncertainties in either end-point or initial-point.

Comparison of Light and Heavy Acetaldehyde.

Tables I and IV give a summary of typical data. Activation energies were calculated from experimental data by the objective method of least squares. The data, compared with those of Fletcher, are given in Table III and plotted in Fig. 1. These values have been corrected for the variation of the actual number of molecules per c.c. as the temperature is varied at constant pressure. This amounts to between + 800 and + 1600 calories. Table IV gives the detailed results for the determination of the temperature coefficient.

TABLE I.—RATES OF REACTION ($\times 10^3$) AT 535° C.

Initial Pressure (mm.).	Light.			Heavy.		
	Initial Rate.	$\tau/_{50}$ %.	$\tau/_{50}$ % Corrected.	Initial Rate.	$\tau/_{50}$ %.	$\tau/_{50}$ % Corrected.
50	1.16	1.50	1.50	0.40	0.59	0.59
100	1.82	2.21	2.21	0.69	0.85	0.85
155	2.14	2.55	2.64	0.90	1.07	1.11
200	2.59	3.08	3.22	0.97	1.32	1.36
300	3.08	3.61	4.17	1.36	1.62	1.82
400	3.83	4.33	5.07	1.57	1.88	2.19

TABLE II.—RATIO OF RATES OF LIGHT AND HEAVY ACETALDEHYDE.

Initial Pressure (mm.).	535° C. Initial Rates.	535° C. $\tau/_{50}$ %.	535° C. $\tau/_{50}$ % Corrected.	550° C. $\tau/_{50}$ %.	520° C. $\tau/_{50}$ %.
50	2.9	2.54	2.54	2.67	2.76
100	2.63	2.60	2.60	2.53	2.59
155	2.37	2.38	2.38	—	2.70
200	2.60	2.36	2.33	2.38	2.57
300	2.27	2.28	2.23	2.34	2.58
400	2.44	2.31	2.30	—	2.55

TABLE III.—ACTIVATION ENERGIES.

Initial Pressure (mm.).	Light (cal.).	Heavy (cal.).
25	55,600 (F.)	57,000
50	55,200	56,400
100	—	56,300
150	53,600	54,500
200	51,000 (F.)	—
250	—	52,800
350	49,100	—
450	48,700 (F.)	49,700

TABLE IV.—TEMPERATURE VARIATION OF RATE.

Light Acetaldehyde.		Heavy Acetaldehyde.			
Temp. (°C.).	<i>t</i> _{50 %} (sec.).	Temp. (°C.).	<i>t</i> _{50 %} (sec.).	Temp. (°C.).	<i>t</i> _{50 %} (sec.).
$(P_0 = 50 \text{ mm.})$.		$(P_0 = 25 \text{ mm.})$.		$(P_0 = 150 \text{ mm.})$.	
575	182	571.2	694	561.2	370
560	324	554.9	1345	548.3	623
545	600	543.7	2089	532.4	1182
530	1135	530.8	3686	517.1	2383
515	2135			515.0	2432
$(P_0 = 150 \text{ mm.})$.		$(P_0 = 50 \text{ mm.})$.		$(P_0 = 250 \text{ mm.})$.	
560	167	570.6	515	550.1	446
550	238	553.3	965	534.5	820
545	295	541.0	1630	518.1	1606
535	469	538.0	1910	506.8	2583
520	832	524.1	3405	494.1	4211
515	1057	511.4	6065		
505	1547	$(P_0 = 100 \text{ mm.})$.		$(P_0 = 450 \text{ mm.})$.	
500	1886	561.6	426	556.7	260
$(P_0 = 350 \text{ mm.})$:		548.8	681	538.3	513
545	196	533.3	1326	517.7	1152
530	362	518.1	2562	483.8	4460
515	643	511.4	3600		
500	1142				
485	2100				

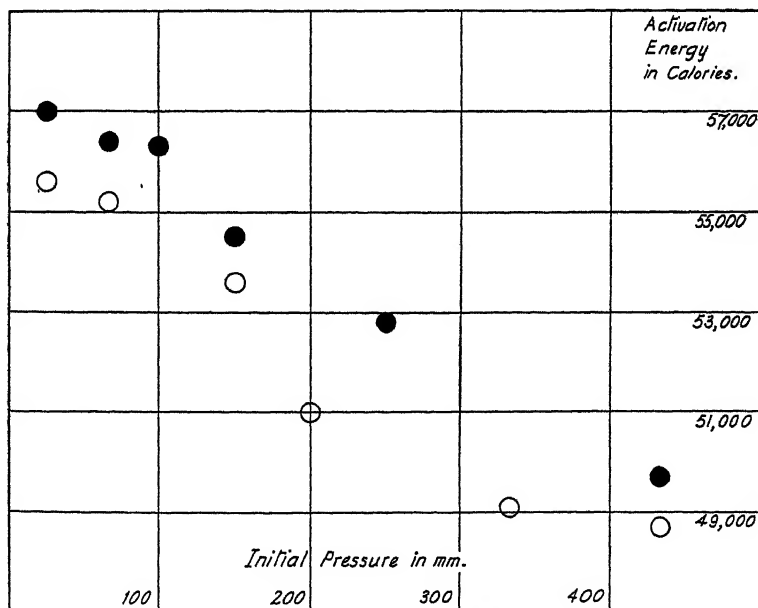


FIG. 1.

Black circles—Deutero-acetaldehyde.
White circles—Normal acetaldehyde.

The deuterio-acetaldehyde is seen to decompose considerably slower than the normal acetaldehyde, the ratio of the rates being nearly 2.5, as often with reactions involving the isotopes of hydrogen. The difference in the zero point energies of the critical bonds is usually from 1000 to 2000 cal., which will at reasonable temperatures account for the above ratio. That there is, in fact, such a difference in activation energy is shown directly by Table III.

The mean ratio of rates would be completely accounted for by a difference of activation energy of 1510 cal. (from results at 550° C.), and 1500 cal. (from results at 520° C.). Eyring and Sherman⁴ calculate the difference of zero point energy of the hydrogen-carbon and the deuterium-carbon bonds as 1100 cal. Temperature coefficient measurements (Table III and Fig. 1) give a mean difference in activation energy of 1000-2000 cal. Experimental error prevents the detection of any variation of this value with pressure.

From the above evidence we can conclude that—

(a) As there is a difference in activation energy nearly equal to the whole of the difference in zero point energy of the C—H and C—D links, it is perhaps unlikely that the major term in E is one concerned with the rupture of the carbon-carbon bond.

(b) If the activation of the carbon-hydrogen bond is the important process the zero point energy difference will account in a consistent manner for at least a large part of the comparison.

There is seen also to be a tendency for the ratio of the rates to increase at lower pressure. This is apparent in all the methods of determining rate and at all the temperatures studied. It suggests that the process is not a single mechanism analogous in the two cases. For example the ratio of two $3/2$ order reactions would be independent of pressure. Again, if there were more than one mechanism, it is not unreasonable to suppose that those involving the longer "time-lags," that is slower and perhaps more complex rearrangements, are relatively the most slowed down by the substitution of deuterium for hydrogen. This would be a reasonable way to account for the varying ratio and would explain also why its actual numerical value is slightly greater than estimated from the zero point energy difference.

Fig. 1 shows the variation of the activation energy with pressure, an effect appearing in both the normal and deuterio-acetaldehydes. It also indicates the existence of more than one mechanism. The fact that the low pressure mechanisms have a greater activation energy can be explained. As these have a longer time lag it might be supposed that this interval involves the transfer of energy from degrees of freedom in a part of the molecule remote from the critical bond. As the actual break-up will utilise only a portion of the energy in these degrees of freedom the average activated molecule will have a greater activation energy than in the simpler mechanisms.

Specific Effect of Ethylene.

Ethylene was purified by fractionation from a liquid air trap. Table V shows a comparison of typical runs. Table VI shows the results of three comparisons at temperatures near to 550° C., rates being measured by the time for 50 % pressure increase.

⁴ *J. Chem. Physics*, 1933, 1, 348.

The reaction of the acetaldehyde is within the error of experiment independent of the presence of the ethylene. In the ethylene oxide-stimulated radical chain decomposition of acetaldehyde, it was found by Fletcher and Rollefson that similar proportions (100 mm. CH_3CHO -100 mm. C_2H_4) reduced the rate to 31 % of the original. Hence this experiment shows the absence of effective quantities of free radicals in the ordinary thermal decomposition.

Specific Effect of Ethane.

Ethane was purified by fractionation from a liquid air trap. Runs of the following composition were then observed for forty minutes: (1) 100 mm. pure ethane, (2) 25 mm. pure acetaldehyde, (3) a mixture of these two. The experiment was also repeated using ether instead of acetaldehyde. Table VII gives a summary of typical results. A comparison of the last two columns will show the effect of the interaction with the ethane.

It can be seen from the above data that the acetaldehyde in the presence of ethane proceeds to the same end-point with unchanged velocity. This shows that (a) the radicals, if such exist in the reaction, are too few in number to effect appreciably the ethane, a gas known to decompose partly by a radical chain; (b) the ethane by its thermal energy is unable to accelerate the activation of the acetaldehyde. In the analogous ether experiment the velocity of reaction of the mixture is greater than the sum of the separate velocities. This effect, though small, was found to be consistently positive. From this we conclude either that the ethane activates the ether or that it suffers a decomposition due to the radicals from the ether. The latter is certainly the most likely as radicals are known to exist in the ether decomposition. A similar influence on the acetaldehyde would be probable if it decomposed by a radical chain. However, the evidence shows that this effect is not present.

Specific Effect of Carbon Dioxide.

Carbon dioxide was prepared by gently heating a tube containing sodium bicarbonate and a layer of phosphoric oxide, all air having been

TABLE V.

Time (min.).	Pressure Increase.	
	200 mm. CH_3CHO (mm.).	200 mm. CH_3CHO + 200 mm. C_2H_4 (mm.).
1	52	54
2	83	83
3	102	101
4	115	113
5	125	122
6	132	129
7	137	133
8	142	137
9	145	141
10	147	143

TABLE VI.

Pressure CH_3CHO (mm.).	Pressure C_2H_4 (mm.).	$1/50\% \times 10^3$.
205	—	5.49
205	—	5.44
205	109	5.55
51	—	2.16
51	—	2.22
51	101	2.16
196	—	6.10
196	—	6.13
196	195	6.17

TABLE VII.

Time (min.).	Pressure Increase in mm.			
	(1) Ethane.	(2) Acetaldehyde.	(1) + (2).	(3) Mixture.
4	0.7	6.1	6.8	6.0
8	1.3	9.3	10.6	10.1
12	1.8	11.5	13.3	13.3
16	2.3	13.2	15.5	15.5
20	2.8	14.4	17.2	17.4
24	3.3	15.6	18.9	19.2
28	3.8	16.1	19.9	20.3
32	4.5	16.7	21.2	21.5
36	4.9	17.4	22.3	22.3
40	5.5	17.8	23.3	23.3

Time (min.).	Pressure Increase in mm.			
	(1) Ethane.	(2) Ether.	(1) + (2).	(3) Mixture.
4	0.7	13.8	14.5	15.3
8	1.3	22.6	23.9	26.2
12	1.8	30.4	32.2	34.3
16	2.3	35.8	38.1	40.3
20	2.8	39.6	42.4	45.0
24	3.3	42.1	45.4	48.6
28	3.8	44.3	48.1	51.6
32	4.5	46.0	50.5	53.8
36	4.9	47.2	52.1	55.5
40	5.5	48.4	53.9	57.0

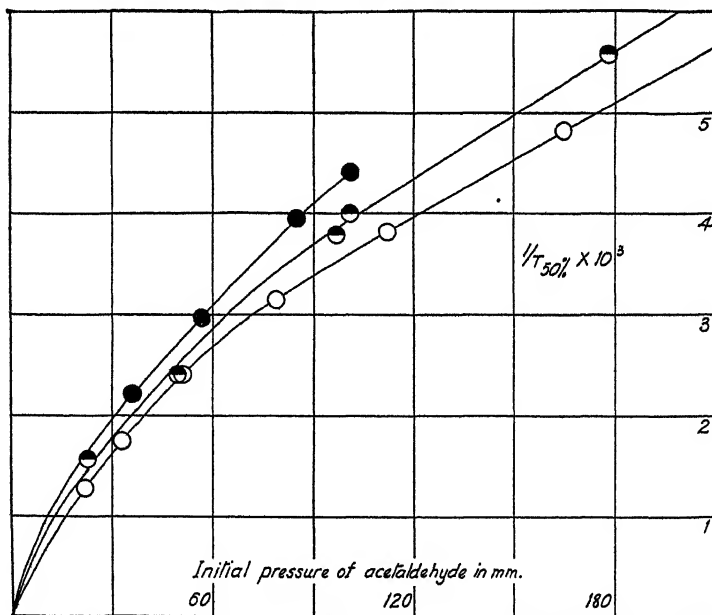


FIG. 2.

Black circles—5-1 Carbon dioxide mixture.
 Half-black circles—2-1 Carbon dioxide mixture.
 White circles—Pure acetaldehyde.

removed by evacuation and washing with the first samples of gas. Rates were measured by the reciprocal of the time for 50 % pressure increase: the results obtained at 555° C. are given in Table VII and in Fig. 2.

The carbon dioxide gives a slight increase in the velocity of the decomposition, which in spite of the large proportion amounts only to about 20 % and 10 % in the two mixtures investigated above. In the case of nitrous oxide the same proportions of 2-1 of carbon dioxide increase the reaction rate to nearly three times the original. This comparatively high efficiency in activation is explained by the similar electronic structures of the carbon dioxide and the nitrous oxide molecules which enables the energy to be readily transferred. Not having this in common with the acetaldehyde, the carbon dioxide would be expected to have a rather less pronounced influence. That the effect is as small as observed demonstrates the highly specific nature of the activation process.

TABLE VIII.

P_0 (mm.).	$t_{1/50\%} \times 10^3$.
5-1 Mixture.	
36	2.22
56	2.96
84	3.75
88	4.17
101	4.40
2-1 Mixture.	
23	1.57
50	2.39
97	3.79
100	4.00
178	5.32
Pure Acetaldehyde.	
22	1.28
33	1.75
51	2.41
79	3.15
112	3.82
165	4.82

The Effect of the Products.

The effect of the products on the reaction velocity was studied by two methods. In the first method the products of previous runs which had gone to completion were premixed with acetaldehyde. The reaction rate was determined by the reciprocal of the time for 50 % pressure increase. The results are shown opposite.

TABLE IX.

Pressure CH_3CHO (mm.).	Pressure Products (mm.).	$t_{1/50\%} \times 10^3$.
50	—	2.49
50	—	2.44
50	—	2.56
50	80	2.50
50	80	2.47
100	—	4.38
100	—	4.52
100	160	3.89
200	—	5.92
200	—	5.74
200	200	5.10
200	200	5.40

In the second method several runs at different pressures were followed to completion. By comparing the rate of the reaction as determined at different stages of these runs with that determined from the initial rate of an equivalent amount of acetaldehyde without products, the effect of the accumulating products in the former case could be shown. Table X shows the comparison at 520° C.

The effect of the products is small. There is, however, a tendency for their presence to cause a slight retardation, the mean value of this

obtained by the first method above being only 7 %. It is difficult to account for this effect. If the reaction were a chain mechanism a shortening of the chain as a result of interference by the products would explain the inhibition. However, as insufficient radicals are present to make the chain breaking of the ethylene of appreciable magnitude it is unlikely that the carbon monoxide or methane molecules should do so. Another explanation is possible if one assumes an occasional activation of the acetaldehyde by the newly formed molecules of product. This need

TABLE X.

Partial Pressure of Acetaldehyde remaining at Given Stage of Run (mm.).	Initial Rate for Corresponding Initial Pressure.	Actual Rate During Run. (In Presence of Products.)		
		(150 mm. Run).	(250 mm. Run).	(350 mm. Run).
350	1.71	—	—	1.71
300	1.57	—	—	1.60
250	1.44	—	1.44	1.46
200	1.30	—	1.31	1.25
150	1.15	1.15	1.04	1.01
100	1.00	0.85	0.73	0.75
50	0.75	0.4	0.4	0.5

occur only about once in ten decompositions in the normal reaction to account for the observed inhibitions. Although the existence of long energy chains is considered to be very exceptional it is perhaps not too much to suppose that a tendency of a magnitude as small as the above should be present in the acetaldehyde. As the presence of an accumulating amount of product would deactivate product molecules immediately after their formation this additional rate would be readily inhibited.

The author is very grateful to Professor C. N. Hinshelwood for continual help and advice during the course of this work.

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HYDROLYSIS OF BENZOIC AND RELATED ESTERS IN VARYING MEDIA.

By R. A. HARMAN.

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The alkaline and the acid hydrolyses of benzoic esters were studied by Newling and Hinshelwood,¹ and by Timm and Hinshelwood.² By finding the velocity constant k at a series of temperatures, they measured in each case the activation energy E and the temperature-independent factor PZ in the equation

$$k = PZe^{-E/RT}.$$

¹ *J.C.S.*, 1936, 1357.

² *Ibid.*, 1938, 862.

It was thus possible to compare quantitatively the effects of different substituents in the benzene ring; and through the comparison to come to some general conclusions as to the mechanism of the hydrolysis.

It was found that in alkaline hydrolysis, the principal effect of the substituent is on the activation energy, electron sinks in the ring lowering this energy by several thousand calories; and electron sources, raising it correspondingly. The analysis of Hinshelwood, Laider, and Timm³ shows that when, as here, an ion is the attacking reagent, such changes in the energy, due to a substituent, depend principally on changes in the energy required for the approach of the attacking reagent. The results of the experiments referred to above are then in the sense to be expected.

In acid hydrolysis, the attacking ion is positive instead of negative, yet substituents produce effects, smaller in magnitude, but in the same sense as before. In this case, $\log_{10}PZ$ has still roughly the same value, but it now shows a correlation with E which was not found in alkaline hydrolysis. The sense of the effects in acid hydrolysis suggests that the addition of OH^- from water molecules at carbonyl carbon is the most important step. The approximately constant value of PZ throughout the hydrolyses is not inconsistent with the Lowry mechanism.

Tommila and Hinshelwood⁴ extended the research by studying the acid and alkaline hydrolyses of substituted phenyl acetates and benzyl acetates; they compared the results for these related types with those for substituted benzoic esters. Although the ring with its substituents is now attached directly to the ethereal oxygen, it still appears that the important step of the reaction, alkaline or acid, is the addition at the carbonyl carbon.

The "transmission coefficient," α , of each of the new structures was also measured. [$\alpha = \Delta E$ produced by a substituent in the new structure divided by ΔE produced by the same substituent in benzoic ester.] α for phenyl acetates was found = 0.71; for benzyl acetates, 0.36 (alkaline hydrolysis).

In the present paper, the transmission coefficients relative to benzoic ester have been determined for two more related structures: phenyl-acetic esters and cinnamic esters. As a second problem, the effect on the alkaline hydrolysis of benzoic ester and of *m*-nitro-benzoic ester produced by changing the solvent has also been studied. Here water is itself a reactant; hence the effect of varying the water might be of special interest. Further, it is perhaps interesting to see whether the usual correlation of $\log_{10}PZ$ with E , found in a changing solvent, will appear.

Experimental.

The experimental method was in general that described by Tommila and Hinshelwood.⁴ The acetone used as solvent was purified by several days' drying over potassium carbonate, and subsequent slow distillation through a 4 ft. column. Absolute alcohol was used for the alcohol-water solvents; and all water was boiled to remove carbon dioxide. The esters were purified to constant M.P. or B.P.; their purity being checked by complete hydrolysis with excess alkali.

It was found difficult to purify the *p*-amino-phenylacetic ester; the ester hydrochloride (prepared from the acid produced by reduction with hydrogen sulphide of *p*-nitro-phenylacetic acid in strong ammonium hydroxide) was therefore used. In the hydrolysis, enough alkali was

³ *J.C.S.*, 1938, 848.

⁴ *Ibid.*, 1801.

used to liberate the free ester, and to provide an excess exactly equivalent to it.

The actual hydrolyses were carried out by mixing equal strength solutions (0.1 N.) of ester and sodium hydroxide, the "standard" solvent being 40 c.c. of water made up to 100 c.c. with acetone. The methods

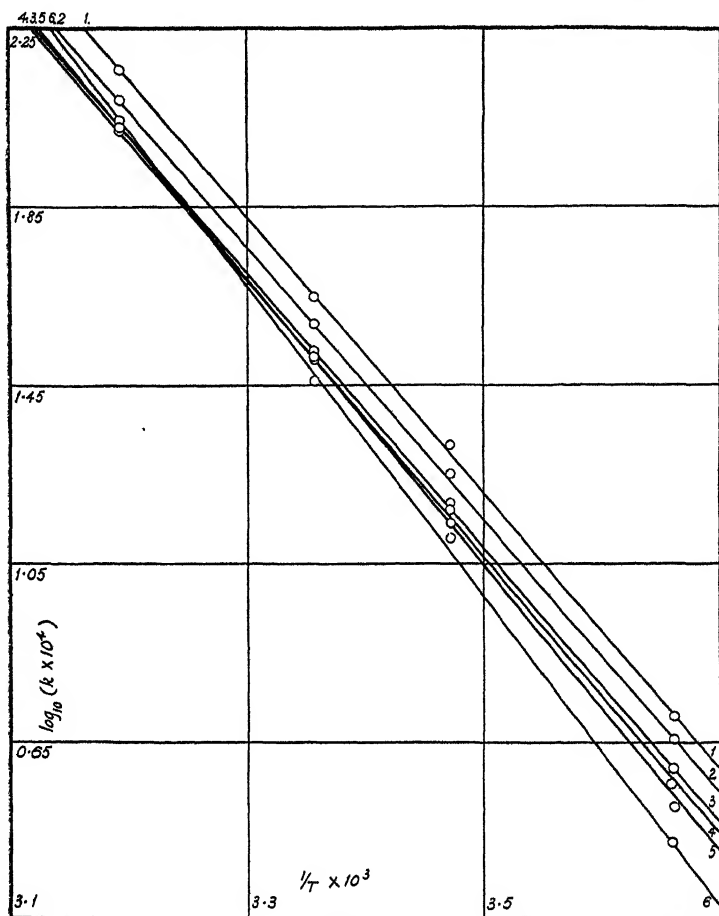


FIG. 1.

Typical Arrhenius lines: Benzoic ester hydrolysed in acetone-water solvents						E (cal.)
1.55	c.c. of water per 100 c.c. of solution	13,820
2.50	" " " "	"	"	"	"	13,970
3.45	" " " "	"	"	"	"	14,070
4.40	" " " "	"	"	"	"	14,330
5.35	" " " "	"	"	"	"	14,880
6.30	" " " "	"	"	"	"	15,840

used for the mixing, for slow and for fast reactions, were the same as those of Tommila; all glassware was standardised, and timing was by stop watch when necessary. The course of the reactions was followed by adding excess acid to a measured sample and back titrating with cresol red as indicator.

The Arrhenius lines for each reaction were obtained by measuring about six values of k at each of four, sometimes five, temperatures. The range of reaction was in general from about 20 % to 60 %; and the range of temperature, about 40°. [Temperatures used were from -20° to 40° , and varied by $\pm 0.1^{\circ}$ at most.] Good agreement was found among the k 's at given temperature, and the linear relation to be expected from the Arrhenius equation was well obeyed.

p-Nitro cinnamic ester formed super-saturated solutions below 25° even when the ester was at half the usual strength, and only 20 c.c. of water was used in the acetone solvent. To compensate for the lessened accuracy, an unusually large number of values of k was measured.

In the study of the solvent effect, it was found that acetone-water-alkali solutions containing less than 40 c.c. of water per 100 c.c. suffered a considerable reaction during the course of their preparation. The acetone-water reaction mixtures were therefore always made up from alkali solutions with at least 40 c.c. of water, and ester solutions with correspondingly less. The constant k 's then obtained indicate that the side-reaction was thus eliminated; measurement showed no appreciable volume change on mixing the non-identical solutions.

The values of k were calculated by assuming a bimolecular reaction between ester and alkali; correction was made for the change in volume of the solvent with temperature, and for any carbonate ion in the alkali, for this ion does not take part in the hydrolysis. E , and $\log_{10} PZ$, were calculated by the method of least squares. The absolute accuracy of the measurements may be judged by comparing the value of E found for benzoic ester with that found by Fairclough and Hinshelwood⁵ and that found by Tommila: 14,330 cal. compared to 14,010 cal. and 14,560 cal. But that the relative values are more accurate may be inferred from the fact that smooth curves are found for ΔE against % water in the solvent, even in a case like that of *m*-nitro-benzoic ester in acetone-water solvents, where ΔE between consecutive values is less than 100 cal.

TABLE I.—THE EFFECT OF STRUCTURAL ALTERATION.

Ester.		E .	$\log_{10} PZ$.	$k_{25^{\circ}}$ $\frac{\text{litres}}{\text{g. mol. sec.}}$
	Benzoic	14,330 cal.	8.06	3.260×10^{-3}
	Phenylacetic	11,310 "	6.95	4.43×10^{-2}
<i>p</i> . NO ₂	"	11,300 "	7.73	2.58×10^{-1}
<i>p</i> . NH ₂	"	11,330 "	6.72	2.445×10^{-2}
	Cinnamic	15,100 "	8.85	4.79×10^{-3}
<i>p</i> . NO ₂	"	13,000 "	8.35	6.11×10^{-2}

The results relating to the effects of structural alterations are collected in Table I; and those relating to the solvent effect, in Table II.

Effect of Altering the Structure.

Table I shows that the activation energies for phenylacetic and the substituted phenylacetic esters are all approximately equal; the value of α is thus virtually zero. The energies are the lowest of any in the series benzoic esters, phenyl acetates, benzyl acetates, phenylacetic esters. E for phenylacetic ester practically equals that for acetic ester⁵ (11,600 cal.) Thus, very little effect from the benzyl group is transmitted to the carbonyl carbon, in contrast with what Tommila found for the benzyl acetates, in which the benzyl group is attached only indirectly, through the ethereal oxygen, to the carbonyl carbon. The difference between these two cases may possibly arise from an easy polarisability

⁵ *J.C.S.*, 1937, 538.

of the electrons on the ethereal oxygen. This oxygen will transmit an effect from the alcoholic group to the carbonyl carbon, on the one hand; and on the other hand, a small effect reaching the carbonyl carbon in the phenylacetates may be virtually neutralised by being almost entirely passed on through the oxygen beyond. With benzoic ester, presumably the effect produced at the carbon atom will be so great as to exceed any possible neutralisation, there being naturally a limit to the polarisability of the electrons on the oxygen.

Some support for the view suggested is perhaps to be found in the values for the ionisation constants of benzoic, phenylacetic, and acetic acids. These are 6.6×10^{-5} , 5.6×10^{-5} , and 1.86×10^{-5} . The effect of the benzyl group at the oxygen in these cases is seen to be almost as great as that of the phenyl group, and quite different from that of the

TABLE II.—THE EFFECT OF SOLVENT ALTERATION.

C.c. of aq. per 100 c.c. of Soln.	<i>E.</i>		$\text{Log}_{10} PZ.$		k_{25} .	
	Benzoic Ester.	<i>m</i> -NO ₂ Benzoic Ester.	Benzoic Ester.	<i>m</i> -NO ₂ Benzoic Ester.	Benzoic Ester.	<i>m</i> -NO ₂ Benzoic Ester.
(a) Acetone-water Solvents.						
55	13,820 cal.		7.83		4.57×10^{-8}	
50	13,970 "		7.86		3.86 "	
45	14,070 "	13,140 cal.	7.88	8.85	3.35 "	1.411×10^1
40	14,330 "	13,260 "	8.06	8.91	3.26 "	1.433 "
35	14,880 "	13,330 "	8.46	8.97	3.22 "	1.453 "
30	15,840 "	13,370 "	9.11	9.00	2.865 "	1.463 "
(b) Alcohol-water Solvents.						
60	14,760 cal.		8.36		3.20×10^{-8}	
55	15,330 "		8.68		2.50 "	
50	15,750 "		8.90		2.03 "	
40	16,460 "	14,290 cal.	9.33	9.38	1.47 "	7.32×10^{-2}
30	17,040 "	15,210 "	9.60	9.97	1.13 "	5.94 "
20	17,410 "	15,900 "	9.75	10.41	8.59×10^{-4}	5.07 "

methyl group. This is what would be expected from the argument above.

In contrast with the phenylacetic esters, where *E* is low and α virtually = 0, cinnamic ester has an *E* somewhat higher even than that for benzoic ester, and α is virtually = 1. These facts are evidence that the effect of the phenyl group on the activation energy of benzoic ester (as compared to acetic) is electronic rather than steric. For in cinnamic ester the phenyl group is even farther removed from the reaction centre than in phenylacetic. Cinnamic ester does, however, contain a conjugated bond system, whereas phenylacetic ester does not; the difference between the two would seem then to arise by the transmission of electronic effects in the cinnamic ester. The value for α confirms the possibility of this transmission. And since the results for benzoic ester closely parallel those for cinnamic, the effect here, too, would seem to be an electronic one.

Effect of Altering the Medium.

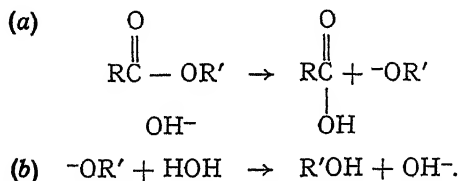
Turning now from the effects of altered structure to those of altered medium (Table II), we find a correlation between $\log_{10} PZ$ and E , approximately of the same degree for both esters in the whole range of media. For a given ester, the line showing the correlation in the acetone-water solvents is practically continuous with that for the alcohol-water solvents. Substitution of alcohol for acetone seems, then, equivalent to reducing the $[H_2O]$ in the acetone.

The actual changes of E for *m*-nitro-benzoic ester in the acetone-water solvents are very small. The transmission coefficient α is at high water concentration greatest in the alcoholic media; but at lower concentrations, greatest in acetone. The energies themselves are higher in alcohol than in acetone solutions. (In acid hydrolysis, Timm found that α is again greatest in the alcohol-water medium containing the standard 40 % of water (by vol.). He also found that E for acid hydrolysis is lower in the alcohol than in the acetone solvent.)

A final point to be noted is that the Arrhenius equation is closely satisfied for all solvent compositions; and that in some of the acetone-water solutions of benzoic ester, E is lowered by the addition of water, yet at 40° the reaction actually goes more slowly than before. This must mean that for each solvent composition, there is a reaction mechanism of characteristic E and P ; those mechanisms with higher E and P being actually excluded.

These characteristic mechanisms might possibly arise as a result of a continuous change in the pattern of the solvent molecules. As $[H_2O]$ is reduced in the solvent, more and more energy might be required to free the reactants from their places in each succeeding solvent pattern; and the entropy increase resulting from breaking up each pattern might rise simultaneously. A correlation between P and E would then appear.

It is, however, rather surprising that such a characteristic pattern should be found for each composition of the solvent; another possible "exclusion mechanism" might conceivably arise if a modified transition complex is characteristic of each solvent composition. In those solvents with the lowest E values, the transition complex might require for its formation the simultaneous co-operation of all three of the various conditions required for reaction—approach of the ion, bond-stretching, and addition of water. When $[H_2O]$ is reduced, the reaction may become more and more dependent on the bond-stretching step alone, as the rate-determining step, (a); with the others following almost automatically, (b):



The co-operation of the step in which water is added is now lost, hence E is higher; but the process of reaction is now simplified and reaction is less dependent than before on accidentally favourable circumstances; P is therefore higher as well.

In comparing acetone with alcohol solvents, it is necessary to suppose that OH^- ions are less available in alcohol than in acetone; that without

the help of the OH^- ion more bond-stretching is then required in alcohol, and that E and P are thus higher in the alcohol solutions than in the acetone.

These ideas provide an explanation of the $\log_{10} PZ - E$ correlation found by Timm to accompany substituent change in acid hydrolysis. Here the most important step would seem to be the stretching of the

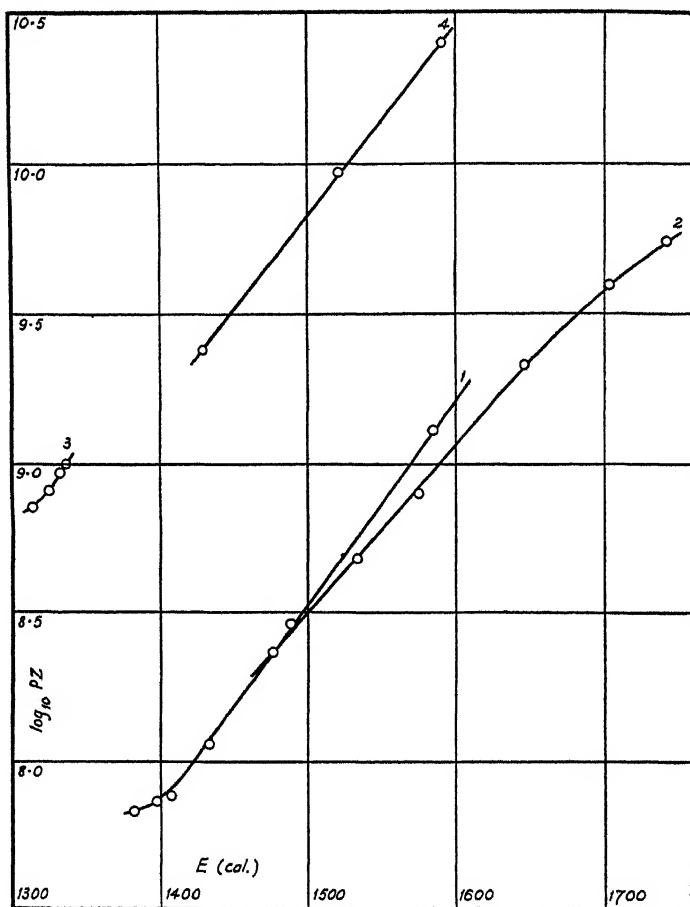


FIG. 2.

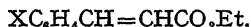
$\log_{10} PZ - E$ correlation				Slope.
1.	Benzoic ester in acetone-water solvents	.	.	0.00066
2.	" " in alcohol-water "	.	.	0.00057
3.	<i>m</i> -Nitro-benzoic ester in acetone-water solvents	.	.	0.00061
4.	" " " in alcohol-water "	.	.	0.00064

bond which must occur before the carbon atom will accept an OH^- from water. The easier this addition, the more nearly is reaction achieved by a simultaneous co-operation of all the steps; thus the lower is E , but also the lower is P , as suggested above. The same arguments can also be extended to describe the effects of substituents on P in alkaline hydrolysis.

As to the solvent effects on α , these may perhaps be understood if it is remembered that a substituent can lower the energy required for approach of the ion, and that at the same time, the addition of water (at the appropriate nucleus) may be indirectly facilitated by the approach of the ion. Thus α should be greatest where approach is easiest; this conclusion holds for alcohol solutions in acid hydrolysis, and for acetone solutions at the lower water concentrations in alkaline hydrolysis. That at higher water concentrations in alkaline hydrolysis, α is greater in alcohol than in acetone would seem to show that in acetone, the approach of the OH^- ion, even for the unsubstituted ester, is close enough to make the addition of water not very difficult; the substituent therefore does not have as full an effect here as in alcohol. When the water concentration in acetone solvents is reduced, however, the full effect of the substituent comes into play, and α rises to surpass its value in alcohol.

Summary.

The constants of the Arrhenius equation have been measured for alkaline hydrolysis of esters of the types $\text{XC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{Et}$ and



It is found that the transmission of electronic effects to the carbonyl carbon atom is less evident in the phenylacetic esters than in any others of the series benzoic esters, phenyl acetates, benzyl acetates. (Types $\text{XC}_6\text{H}_4\text{CO}_2\text{Et}$, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{X}$, $\text{CH}_3\text{CO}_2\text{CH}_2\text{C}_6\text{H}_4\text{X}$). But in cinnamic esters the transmission is about as great as in benzoic esters.

The solvent effects on benzoic and on *m*-nitro benzoic ester hydrolysis (alkaline) have also been studied. As the solvent composition is altered, the usual correlation of $\log_{10}\text{PZ}$ with *E* is found. The effect on *E* produced by the substituent, too, is found to vary with solvent composition.

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REVIEWS OF BOOKS.

Metallography. By C. H. DESCH, D.Sc., Ph.D., F.R.S. 4th Edition, 1937. (London: Longmans, Green & Co. Pp. viii + 402. 21s. net.)

Introduction to Physical Metallurgy. By L. R. VAN WERT, S.D. (New York and London: McGraw-Hill Book Co., Inc. 1937. Pp. ix + 292. 18s. net.)

These two books deal essentially with the same subject and yet are in many ways totally unlike each other. Dr. Desch's book is well known to most students of metallography in this country. It has been revised thoroughly, but apart from this, follows the general plan which has proved so successful in the earlier editions. It gives a thoroughly good account of the fundamental concepts of metallography, and we have no doubt that many students in the future, as others have done in the past, will endeavour to assimilate its contents as an essential part of their studies for metallurgical degrees and diplomas.

The other book is on a different footing. The author states in his preface that it is "an outgrowth of a course of lectures" given at Harvard

University, those taking the course being post graduate students in the Graduate School of Engineering and certain undergraduate students with more diverse interests, the former predominating. As a result of the needs of this rather heterogeneous group, the author has evolved a text-book which is intended to be "sufficiently specific and fundamental for those who were to continue in the science, yet interesting and comprehensive enough for those seeking a general knowledge of the subject and whose active acquaintance with it would likely end with the course." Such was the author's intention, and so far as writing an interesting book is concerned he has succeeded in his object; whether, however, it contains the right sort of information to give to a mechanical engineer who may not study the subject further, believing that he has imbibed such knowledge of physical metallurgy as he may require for his work, is quite another matter.

After a brief introduction, the author sets out to answer the question, "What is a metal?" and in the course of an interesting chapter leads up to some generalisations which seem to require hedging round with a number of limitations. For example, "a well developed capacity to flow plastically . . . is a property of crystalline substances . . . presumably because of the peculiar manner of response of such substances to an applied stress" may be true of most metals, but not of many inorganic compounds which are equally crystalline; in fact, plasticity is one of the last properties one would associate with most non-metallic crystals!

The other chapters deal in sequence with metals and their properties, the equilibrium diagram (two chapters), the micro-constituents of alloys, the properties of alloys and, finally, the mechanical and thermal treatment of metals and alloys. The book is interestingly written, in fact, one might suspect that the author's object has been to provide an attractive collection, with a popular appeal, of all sorts of metallurgical information, rather than a logically developed account of the fundamental facts of physical metallurgy. There are a number of minor errors, but doubtless these will be corrected if and when a further edition is required.

Annual Reports on the Progress of Chemistry, xxxv, 1938. (London, The Chemical Society. Pp. 447. Price 13s. net, post free.)

The Annual Reports are always eagerly awaited. They are of invaluable assistance, and on some aspects of chemistry a perusal of a few years' reports on special subjects provides unique information, which has not yet found its way into the text-books.

The present volume maintains the traditionally high standard. The reports on General and Physical Chemistry (79 pp.) prepared by Dr. Melville with the collaboration of Drs. Bowden, Roberts and Sutherland, deal faithfully with matters with which readers of these Transactions are specially familiar. But it is impossible so to limit the range of physical chemistry: the section on crystallography (28 pp.) and much of those on organic chemistry (127 pp.) and on analytical chemistry (31 pp.) are of great physico-chemical interest.

Proceedings of the Symposium on the Chemistry of Cements. Stockholm, 1938. (Ingeniörsvetenskapsakademien Stockholm. 1939. Pp. xvi + 578. Price 25 Swedish Cr.)

The proceedings of the symposium on the chemistry of cements held in Stockholm in July, 1938, under the joint auspices of the Royal Swedish Institute for Engineering Research and the Swedish Cement Association have now appeared in a well-produced volume, written entirely in the English language. The scope of the volume may best be indicated by the titles of the papers which are as follows: "Constitution of Portland Cement Clinker" (Dr. R. H. Bogue, U.S.A.); "X-Rays and Cement Chemistry" (Dr. W. Büssem, Germany); "The Calcium Aluminate and Silicate Hydrates" (Mr. G. E. Bessey, Great Britain); "The Calcium Aluminate Complex Salts" (Mr. F. E. Jones, Great Britain); "Portland Cement and Hydrothermal Reactions" (Professor T. Thorvaldson, Canada); "Effect of Water on Portland Cement" (Professor P. Schläpfer, Switzerland); "The Chemistry of Retarders and Accelerators" (Dr. L. Forsén, Sweden); "The Mineral Content of Aluminous Cement" (Dr. N. Sundius, Sweden); "Reactions of Aluminous Cement with Water" (Dr. G. Assarsson, Sweden); "The Chemistry of Pozzolanas" (Dr. F. M. Lea, Great Britain); and "The Physical Structure of Hydrated Cements" (Mr. S. Giertz-Hedstrom, Sweden). In addition to these papers and the discussions thereon, the volume contains two introductory papers by The. Svedberg and Professor J. A. Hedvall entitled respectively "The Study of Giant Molecules by means of Ultracentrifugal Sedimentation, Diffusion and Electrophoresis" and "Reaction between Substances in Solid State with special regard to Systems containing Silica."

In general, the papers may be described as critical surveys including in varying degree previously unpublished work. A study of these papers and of the many valuable contributions to the discussion gives an excellent indication of the great progress made in this branch of applied science since the Faraday Society held a general discussion on the Setting of Cements and Plasters in January, 1918. Intensive phase equilibrium studies combined with microscopic and X-ray investigations have now yielded a well-developed picture of the mineralogy of Portland cement clinker though certain complications introduced by partial non-crystallisation of the liquid formed at the clinkering temperature, and by minor components such as the alkalis, still remain to be disentangled. This advance in knowledge has now been reflected in the practice of cement manufacture by the development of cements with special properties. Even the very complex problem of the constitution of aluminous cement is yielding to attack by similar methods. The value of the improvements which have been made in the technique of the preparation and etching of polished clinker surfaces, and of polished and etched thin sections which can be examined both by transmitted and reflected light, is well brought out and special tribute may be paid to the photomicrographs reproduced in Tavasci's contribution to the discussion on aluminous cement.

Knowledge of the hydration of Portland cement and of the hydrated cement compounds has lagged behind that of cement constitution, but the chemistry of the complex series of hydrated calcium aluminate and silicate compounds is now becoming clearer, though it is evident from the

papers and discussion that this remains a controversial field. In the use of Portland cement the satisfactory control of setting time is essential, but the mechanism of the retarding or accelerating action of different salts has been obscure. Though future work may possibly show that modification is required in points of detail, the theory advanced in Forsén's paper to explain normal and rapid setting provides a general explanation of the apparently unrelated effects of numerous different agents. The increasing use made of pozzolanic additions to cements has in recent years stimulated interest in the chemistry of these materials, but the subject as a whole, does not appear to be so advanced as in the case of cements. Set cements, consisting as they do of inhomogeneous solids containing not only solid and liquid phases, but also water held under the action of surface forces, do not provide an easy field for investigation, and the difficulties are increased by the change in properties with time. It is not therefore surprising to find that the theory of properties of set cements such as the reversible volume change on wetting and drying and plastic flow under load still remains controversial. In view, however, of its technical importance, it seems likely that the study of the physical structure of set cements must now receive increased attention.

The proceedings of the Stockholm Symposium, presenting as it does a well-balanced picture of the present state of knowledge, is worthy of the attention of all interested in this field of chemistry, while to cement specialists it will be essential.

F. M. L.

Thorpe's Dictionary of Applied Chemistry. Fourth ed. Vol. III. CHEMICAL CALCULATIONS—DIFFUSION. By SIR J. F. THORPE & M. A. WHITELEY. (London: Longmans, Green. Pp. xxiii + 608. Price 3 guineas.)

This volume replaces 352 pages from the third edition; apart from the pages devoted to new entries, very many of the articles in the last edition have grown in size in the course of being brought up-to-date.

Among the new entries, some of which appeared in part in the two Supplement volumes to the third edition, are Chemical Calculations (6½ pp.), Chemical Warfare (15 pp.), Chemiluminescence (1½ pp.), Chlorophyll (5 pp.), Co-ordination Compounds (9½ pp.), Cyclences (4 pp.), Deuterium, with a useful section on exchange reactions (7 pp.), and Diacetylenes (1½ pp.).

The majority of the other articles, also, seem to have been rewritten, some being expanded very considerably. Notable examples are: Chromium (11 to 20 pp.), Clay (5-10 pp.), Cinchona alkaloids (26-51 pp.), Coke manufacture (12-18 pp.), Colloids (4½-15 pp.), Colorimeters, etc. (4½-11 pp.), Condensers (2-8 pp.), Corrosion of Metals (17-32 pp.), and Crystallisation (¾-9½ pp.). Mere bulk is, however, no guide. The important thing is that these articles are, in fact, really useful and up-to-date summaries of information.

The article on Corrosion of Metals: Protective Measures, contains 1¼ columns on "electro-deposited coatings" and the article on Chromium has ¾ column on electro-deposition, neither of which was in the last edition; it is to be hoped that the 7 pp. main article on Electrodeposition will not

be found missing from the next volume, for this is surely a subject of sufficient importance to warrant special treatment.

The present volume does not give much scope for purely physico-chemical articles, but those which have been noted are well done. We may perhaps be permitted to say that, by the year 1939, some attempt might have been made to ensure compliance with the Joint Committee's recommendations as to physico-chemical symbols. There need be no fear as to inconsistency with earlier volumes, because there is, indeed, no consistency at present, except a perverse tendency to put physicochemical symbols in roman and mathematical in italic type—without, however, becoming hidebound, as we find on page 605—

$$D = \frac{k}{\alpha} \sqrt{pT} \cdot e^{-\frac{E}{RT}}.$$

We repeat our plea (*This vol.*, 297) for an *ad hoc* index.

Rutherford. BEING THE LIFE AND LETTERS OF THE RT. HON. LORD RUTHERFORD, O.M. By A. S. EVE. With a Foreword by EARL BALDWIN OF BEWDLEY. (Cambridge University Press, 1939; pp. xvi and 451 and 17 plates. Price 21s. net.)

The vast amount of work carried through in Rutherford's all too brief life, its profound influence on physical and chemical thought and the vivid personality of the man himself are not readily described within the comparatively short space of 451 pages. Dr. Eve has accomplished this task in noteworthy fashion and has produced a volume of outstanding interest, not only to those who knew Rutherford the man and his work, but also to all who care to read a vivid human story. There is scarcely a page which requires a knowledge of modern physics for its understanding.

Professor Eve, at one time a colleague of Rutherford and a successor in his chair at McGill, was singularly well fitted for this labour of love, and he has shared with us all his good fortune in having access to the letters written by Rutherford to his wife and his mother and to many colleagues in all parts of the world. We may all rejoice, too, that Rutherford was blessed in having a mother and a wife who from his boyhood days must have realised that their man was destined for great things and kept his letters.

Rutherford has therefore been allowed in large measure to tell by his letters his own life story. At every stage of his voyage of discovery we find him writing in simple language of the things he has done or intends to do and of all the incidents of his life at Cambridge, at McGill, then at Manchester and finally again at Cambridge. Dr. Eve has very skilfully taken just so much of these letters as is needed to picture every phase of his life, interpolating a paragraph or so here and there to explain simply something which may not at once be intelligible to the reader, or to fill in a gap of a few months where reproduction of correspondence might occupy more space than is warranted if the true perspective of life is to be kept.

It is a very moving story—to the younger reader, especially, a very inspiring one—of the young hero, starting life with scholarships even in his earliest schooldays in New Zealand and then gaining an 1851 Exhibition which sent him to Cambridge to work with "J. J." Graduating with equal

facility in classics, modern languages and science, he attained at the end, as the leader of modern physics—but still, as he would say, “without requiring a larger size in hats”—to the highest honours which man can give, and he will go down in history, an equal, in the noble company of Galileo, Newton, Faraday and such benefactors of mankind.

His boyish enthusiasm appears in every page, whether it be joy in his work or in his many other interests in life. He got a great deal of fun out of it all; there is a joyful chuckle to be found on many a page of his biography. Those who were at this Society's Free Radical meeting in 1933 will remember with delight the after-dinner story of Rutherford and the Archbishop, which is here retold.

Semi-Conductors and Metals. By A. H. WILSON. (Cambridge University Press, 1939.) Pp. viii + 119. Price 7s. 6d. net.

The aim of this book is to give a simplified account of some of the main achievements of the electron theory of metals. Those parts of the theory which for their proper development demand complicated mathematics are discussed in a qualitative way only, and frequent references are made to the author's more detailed treatise (*Theory of Metals*, Cambridge, 1936). Therefore the present book will make an excellent first introduction to the subject for readers who lack the time or the mathematical equipment to work through one of the more substantial text-books.

It is not the purpose of the book to present new points of view, but discuss subjects which have been treated in a more mathematical way elsewhere; we would like to mention nevertheless the interesting chapter on semi-conductors, which seems to us the most complete review of the theory of the subject which has yet appeared in English; and also the useful summary of recent work on thermal conductivity in metals and insulators. The greater part of the book deals with the electronic properties of metals, and thus with the motion of electrons in a crystal lattice, with Brillouin zones, metallic cohesion, magnetism and electrical conductivity. Considerations of space have made it impossible to deal with alloys or with metal optics. It is perhaps a pity that there is no mention of the results obtained from the investigation of the emission bands of soft X-rays, as they give probably the most direct experimental proof of the validity of the fundamental theoretical ideas.

N. F. M.

ERRATA.

Page 1250, line 3 of table in column headed “Simple Cubic” should read:—

$$S_+ = \left(\frac{1}{2}\right)^3 \left[\sum_1 \frac{\rho}{2} + 2 \sum_2 \frac{\rho + 1}{2} + \sum_3 \frac{\rho}{2} \right].$$

Page 1263, line 26 of Section 2b should read

$$0.8 < \theta_1 < 1.0.$$

The Faraday Society.

MINUTES OF THE THIRTY-THIRD ANNUAL GENERAL MEETING.

*Held on Saturday, 11th November, 1939, at 2.30 p.m.
in the Department of Colloid Science, Cambridge.*

1. Before proceeding to the business of the Meeting, the President expressed regret that in the national emergency it had been necessary to postpone the meeting from the 27th September. It was essential, however, to hold the meeting in order that a Council and Officers should be available to carry on the business of the Society, and he appreciated the presence of so many members.

2. The Minutes of the Thirty-second Annual General Meeting were taken as read and confirmed.

3. The Annual Report and Statement of Accounts for the year 1938 were submitted by the Honorary Treasurer. In moving their adoption the Honorary Treasurer expressed his own and the Society's regret that owing to the death of Mr. Emile Mond during the financial year it had fallen to another Honorary Treasurer to undertake this duty. He said that a perusal of the Report and of the Accounts would show that the Society's finances were in a very sound condition. The main revenue accrued from members' subscriptions and from the sales of *Transactions*; the fact that the Treasurer was again able to report so satisfactory a state of affairs showed that success bred success. The Society remained always indebted to the late Lieut.-Col. J. J. Bourke for his legacy, and the Council had ensured that his memory should be perpetuated by constituting the Bourke Fund, of which details would be found in the Report.

The adoption having been seconded by Professor Ferguson, the Report and Statement of Accounts were duly adopted.

4. The President declared the Council for the year 1939/40 to be elected in accordance with the notice convening the meeting as follows :—

President.

PROF. E. K. RIDEAL, M.B.E., D.Sc., F.R.S.

Vice-Presidents who have held the Office of President.

SIR ROBERT ROBERTSON, K.B.E., D.Sc., F.R.S.

PROF. F. G. DONNAN, C.B.E., Ph.D., F.R.S.

PROF. C. H. DESCH, D.Sc., F.R.S.

PROF. N. V. SIDGWICK, Sc.D., D.Sc., F.R.S.

PROF. M. W. TRAVERS, D.Sc., F.R.S.

Vice-Presidents.

PROF. J. E. COATES, O.B.E., D.Sc.	PROF. W. C. M. LEWIS, D.Sc.,
PROF. A. FERGUSON, D.Sc.	M.A., F.R.S.
PROF. R. H. FOWLER, O.B.E.,	C. C. PATERSON, D.Sc., O.B.E.
M.A., F.R.S.	PROF. R. WHYTLAW-GRAY, O.B.E.,
	Ph.D., F.R.S.

Honorary Treasurer.

R. E. SLADE, D.Sc.

Chairman of the Publications Committee.

PROF. A. J. ALLMAND, D.Sc., F.R.S.

Council.

E. J. BOWEN, M.A., F.R.S.	F. D. MILES, D.Sc.
C. R. BURY, B.A.	W. J. SHUTT.
J. J. FOX, O.B.E., D.Sc.	D. W. G. STYLE, Ph.D.
PROF. W. E. GARNER, D.Sc., F.R.S.	PROF. S. SUGDEN, D.Sc., F.R.S.
R. LESSING, Ph.D.	O. J. WALKER, Ph.D.

5. The Secretary, being invited by the President to report upon what it was possible for the Society to do under war conditions, said that the Society was fortunate not only in being financially sound, but also in having its normal office routine. It had been necessary in the early days to ask members to write to his home address as Miss Wakeley was engaged on whole-time national service; she was now, however, able to attend at the office during the usual office hours.

A Note in the issue of *Nature* of 14th October had given some idea of the Society's plans; he wished to dissociate himself, however, from the statement that 8 % of the members were "resident in German territory"—the 8 % included Austrians, Czechoslovaks and Poles. It was obvious that during the war there would be an 8 % drop in subscription revenue. He expressed the hope and belief that, owing to the very real enthusiasm and appreciation of members, this revenue would not otherwise be seriously affected. He asked members, even though with their rising expenses it might be difficult, to continue their support and encouragement of the Society's work.

The usual facilities for obtaining membership of the American Electrochemical Society, the Société de Chimie Physique and the Nederlandsche Chemische Vereeniging would be continued, but owing to foreign exchange difficulties the rate quoted in the subscription notice, to be issued with the December issue of the *Transactions*, could only be retained in force until the 31st December; later applications would have to be subject to the rate of exchange existing at the time of application. During the war, of course, it would not be possible to continue the arrangements for obtaining membership of the Deutsche Bunsengesellschaft.

With regard to publication, he anticipated no difficulty. The Society had a good stock of paper, and the printers were operating as satisfactorily and as speedily as in peace time. He had taken prompt steps, in connection with papers received or sent overseas and, generally,

in regard to the publication of the *Transactions*, to co-operate with the Censor in order to avoid delay in publication. A steady flow of new papers of high standard was being received and the Society might expect a greater number from authors in the Dominions and in friendly and neutral countries; he desired to express, as Editor, his thanks to referees for their collaboration in assisting speedy publication. He felt members would wish that the policy of prompt publication should be continued, and he had no reason to expect difficulty in maintaining the *Transactions*.

It would obviously be impossible to continue General Discussions of the international character for which the Society was so famous. The papers contributed to the proposed September meeting would, however, be published in the new year, and he would see whether a "written" discussion could usefully be prepared and published. If this idea met with success, it might be possible to continue this activity of the Society in some modified form. The Council were about to meet and discuss the Society's general policy during the war.

The President having invited further comments:—

(a) Dr. D. D. Eley asked whether it was not possible for members to obtain the *Journal of Chemical Physics* on special terms. The Secretary said there was at present no such arrangement, but he would make enquiries.

(b) Prof. M. W. Travers and Dr. O. J. Walker expressed the earnest hope that the Society would not abandon the idea of meetings; though such meetings must be different in scope from the "General Discussions," it would be a pity to forego the occasional opportunity of meeting in person and discussing problems of interest. The President expressed his sympathy with the plea, and said the Council would see what could be done.

This concluded the business of the meeting.

NOTICE.

1. At a meeting of the Council held later in the afternoon the Council considered the policy to be adopted by the Society during the war and the steps which could be taken to assist in its prosecution. The following two decisions were made:—

(a) The President stated that the Chemical Society's Advisory Research Council included Professor Donnan, Professor Hinshelwood, Dr. Slade and himself. The Advisory Council felt, however, that in its approach to physical chemists and biochemists, it would feel strengthened and would welcome co-operation with similar committees set up respectively by the Faraday Society and the Biochemical Society. The Council therefore appointed the above-named gentlemen with Professor W. L. Bragg (with power to consult) as the Faraday Society's Advisory Committee on Physical Chemistry, it being understood that the Committee would co-ordinate its activities as it thought desirable with those of the Chemical Society's Advisory Committee.

(b) The Council recognise that it is impracticable to maintain during the war the international character of its General Discussions. They

agree, nevertheless, with the views expressed at the Annual General Meeting that members will welcome an opportunity of meeting one another and of discussion. A Committee, consisting of the President, Professor Travers and Dr. C. C. Paterson, was therefore formed to explore the possibility of arranging a two-day meeting in the Spring for the discussion of "Current Problems of Fundamental Importance." The Committee will also consider and report as to how far it is possible or desirable to co-operate with, *e.g.*, the Federation of British Industries and the Association of British Chemical Manufacturers, and also whether the contributions to such a meeting can be published, having regard to National Interests.

2. The Secretary will greatly appreciate the co-operation of members in remitting their subscriptions promptly, in order that the *Transactions* may be sent to them without delay. Such co-operation is particularly desirable on the part of overseas members and especially of those members resident in continental countries other than France. Some delay is unavoidable if the *Transactions* cannot be sent by the printers as soon as they are published on the first day of each month.

3. The work of the Referees and of the Editor is greatly facilitated if authors will kindly take care in the preparation of their papers to comply as far as possible with the "Instructions to Authors" printed on the back cover of the *Transactions*, and, particularly, to give clear indications to the printer as to the type fount to be used in physico-chemical and mathematical formulæ.

G. S. W. MARLOW.

13 South Square, Gray's Inn,
London, W.C.1.

1st December, 1939.

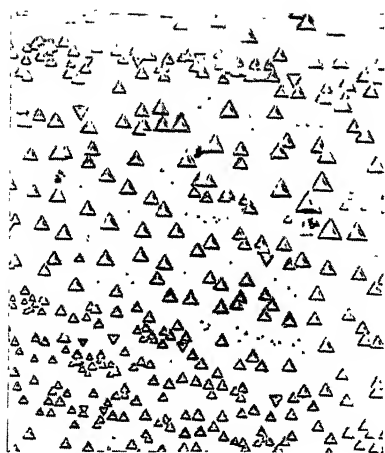


FIG. 1.



FIG. 2.

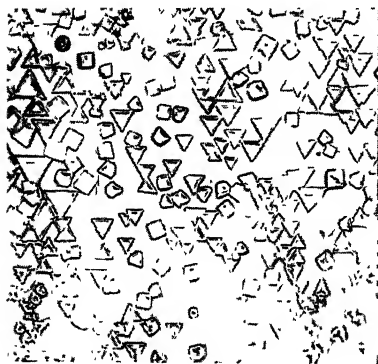


FIG. 3.

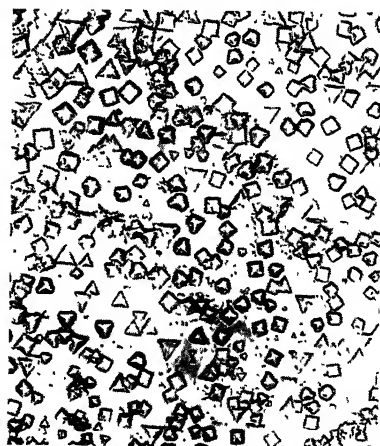
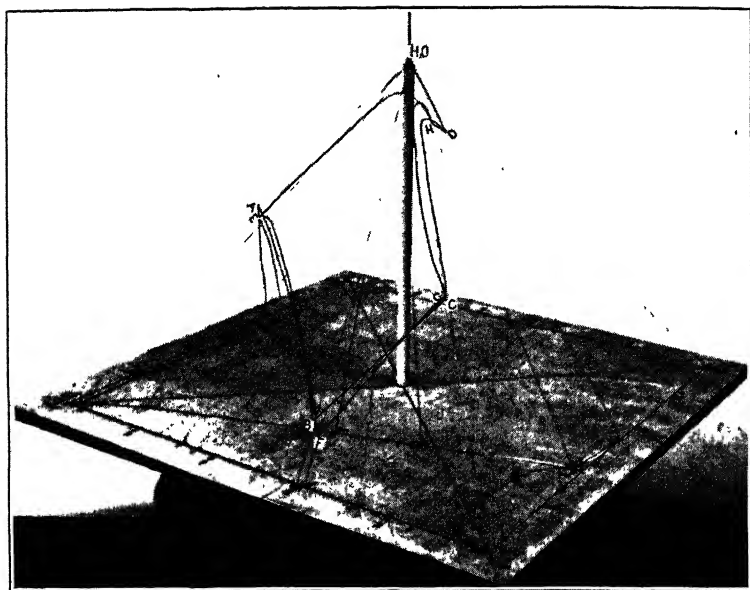
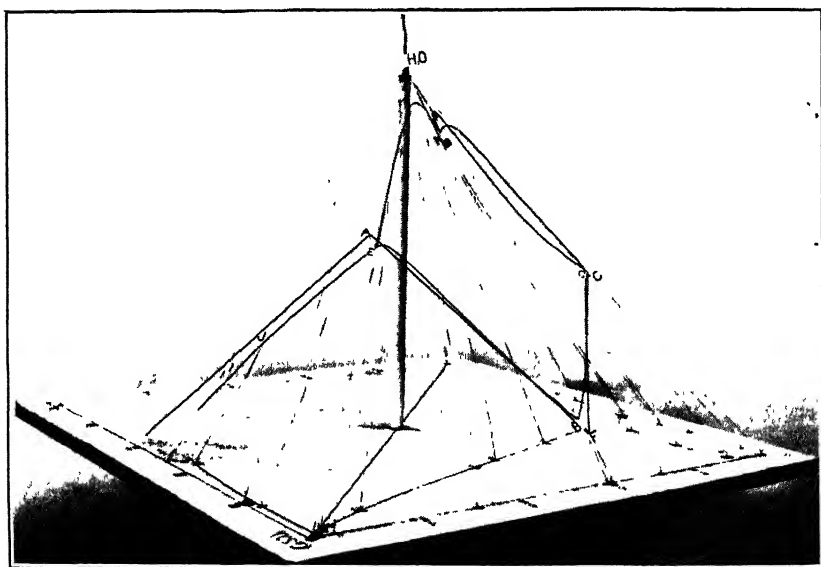


FIG. 4.

[See page 1362.]



(a) From $(\text{CaO})_3$ corner.



(b) From $(\text{CaSO}_4)_3$ corner.

Space model of portion of quaternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$ at 25°C .

[See page 1503.

THE ADSORPTION OF ACETIC ACID BY MERCURY.

By R. C. L. BOSWORTH.

Received 12th June, 1939.

In an earlier report on this subject,¹ the author has recorded measurements on the adsorption of acetic (and other) acids by mercury. These measurements were obtained by means of two independent drop methods, one of which recorded the amount of acid adsorbed directly, the other indirectly through a measurement of the surface tension followed by application of the Gibbs Adsorption Isotherm. The satisfactory agreement obtained between results from these two different methods would seem to indicate that these acids in the adsorbed phase occur in the same molecular form as they do in the vapour phase, and that measurements of surface tension by methods other than the drop-weight method could with confidence be applied to the measurement of adsorption. The drop methods do not lend themselves readily to measurements over a range of temperatures, and in the former work one temperature only (20° C.) was used. By the maximum bubble pressure method, application of which to the problem of the surface tension of mercury has been investigated by Bircumshaw² and by Brown,³ it should be possible to extend the above-mentioned measurements to cover a range of temperatures up to the boiling-point of mercury, and thus to obtain besides the amount of acid adsorbed the corresponding heat of adsorption.

The experimental work consisted in measuring, by the technique already described,⁴ the surface tension of mercury in the presence of air containing varying proportions of acetic acid vapour, and at a number of differing temperatures from 20° C. to 260° C. The acetic acid vapour was mixed with air in the desired proportions by drawing air, after passage through the usual drying and purifying tubes, through a gas bubbler of acetic acid at 25° C., and finally over glacial acetic acid crystals (or liquid) at some lower temperature so adjusted as to give the required partial pressure of acetic acid vapour. For calculation of these pressures the figures given in the International Critical Tables were used. The air containing a known partial pressure of acetic acid vapour was then led in turn through each of a pair of amalgamed copper tips dipping in mercury contained in a hard glass test tube immersed in an oil bath thermostat. Care was taken to ensure that the two tips were kept at the same level and the difference in the pressures required to release the bubble from the wide and narrow jet was recorded as a function of the temperature of the mercury and the partial pressure of the acetic acid. The mercury used was purified by the electrolytic method of Newbury⁵ involving the use of mercurous

¹ R. C. L. Bosworth, *Trans. Faraday Soc.*, 1932, **28**, 903.

² L. L. Bircumshaw, *Phil. Mag.*, 1928, **6**, 510; *ibid.*, 1931, **12**, 596.

³ R. C. Brown, *ibid.*, 1928, **6**, 1044.

⁴ R. C. L. Bosworth, *Trans. Faraday Soc.*, 1938, **34**, 1501.

⁵ E. Newbury, *Industrial Chemist*, 1929, 289.

perchlorate as the electrolyte; and was carefully dried before being placed in the bubbler. The previous experience of the author with this type of measurement has justified the use of amalgamated copper tips.⁴ No trouble was experienced with variable readings due to changes in the contact angle nor was any drift in the readings due to contamination of the mercury by copper compounds noticeable. As in the previous work it was, however, thought desirable to change and re-purify the mercury at frequent intervals.

Results.

As described in the earlier paper on the bubble pressure method the jets were made knife-edged with internal and external radii practically identical. The wide jet had a radius of 0.1995 cm. and the narrow one

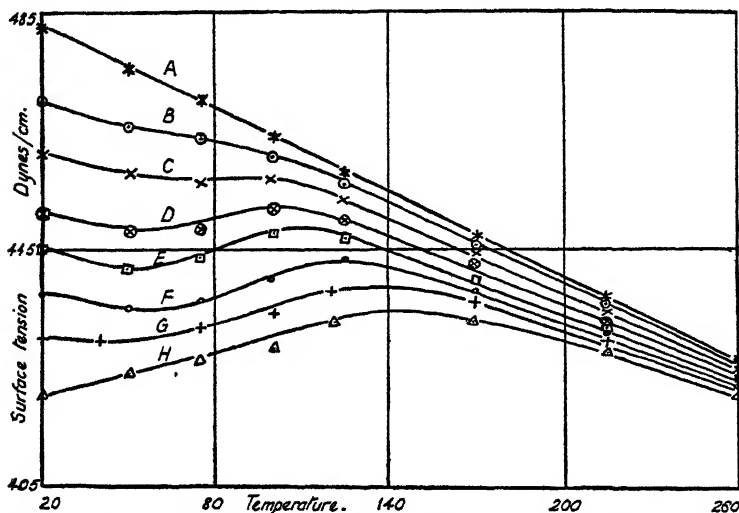


FIG. 1.—Variation of surface tension with temperature in the presence of fixed pressures of acetic acid. Curve A, $p = 0$; B, $p = 0.5$ mm.; C, $p = 1.2$ mm.; D, $p = 2.3$ mm.; E, $p = 3.5$ mm.; F, $p = 5.9$ mm.; G, $p = 8.2$ mm.; H, $p = 11.7$ mm.

0.0985 cm. The recorded pressure differences were converted into surface tension measurements by the method described before.⁴ The variation of γ (the surface tension) with T (the temperature) at fixed p (the partial pressure of acetic acid) is shown in Fig. 1. The partial pressures for which the γ - T curves in Fig. 1 were obtained were: 0.0 mm., 0.5 mm., 1.2 mm., 2.3 mm., 3.5 mm., 5.9 mm., 8.2 mm. and 11.7 mm. It is to be noted that only in the absence of the capillary-active acetic acid vapour is the temperature coefficient of the surface tension constant. At sufficiently high pressures of acetic acid there exists a temperature range over which the surface tension of mercury actually increases with increasing temperature.

From the family of curves shown in Fig. 1, a second family may be drawn as γ - p curves at constant T . Many of these curves will intersect others of the same family, and for this reason presentation of the results as γ versus p curves would not give as clear a picture as the γ versus T curves. For the development of these results $d\gamma/d \ln p$ is required.

This may readily be obtained from the γ - p curves referred to above, or more conveniently by reading off tables of γ versus $\ln p$ at a series of temperatures and calculating the required differentials by means of the calculus of finite differences. The number of acetic acid molecules adsorbed per unit area is then given by σ in the Gibbs adsorption isotherm.

$$\sigma = -1/kT \cdot d\gamma/d \ln p.$$

From this equation σ has been calculated at a series of different values of p and T . The results of these calculations are given in graphical form in Fig. 2.

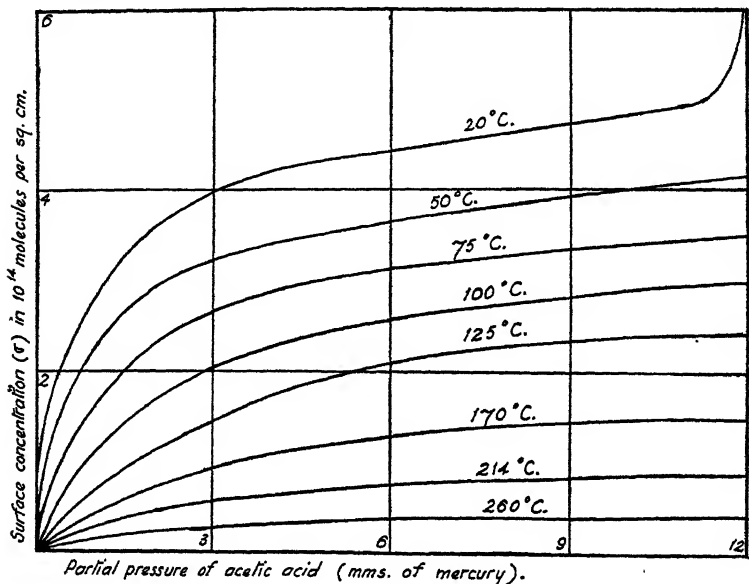


FIG. 2.

This Fig. shows σ plotted as a function of p at a series of selected temperatures: *viz.* 20° C., 50° C., 75° C., 100° C., 125° C., 170° C., 214° C. and 260° C. It will be seen that the amount of acid adsorbed decreases with increasing temperature at all values of p . In other words, the pressure in equilibrium with a film of given concentration increases with increasing temperature. This means, of course, that the adsorption is associated with an evolution of heat and this heat must be re-absorbed before the film can be evaporated. Let us call this heat of adsorption E . Then E is given by

$$E = -1/RT^2 d \ln p'/dT. \text{ Calories per mole.},$$

where p' is the pressure in equilibrium with a film of concentration σ maintained at a temperature $T^\circ K$.

Fig. 3 shows $\log p'$ plotted against $10,000/T$ at a series of fixed values of σ . These fixed values were: 0.25, 0.5, 1, 2, 3 and 4×10^{14} molecules per square cm. At each value of σ the points obtained are satisfactorily colinear. The resultant family of straight lines are not quite parallel, indicating that the heat of adsorption varies slightly with the surface concentration. Table I gives the values of E calculated from the slopes of the lines in Fig. 3.

The heat of evaporation falls with rising surface concentration, and the fall is most marked when the films are dilute. In both these respects the behaviour of these films on liquid mercury is parallel to that of the films formed by oxygen or nitrogen on solid tungsten.⁶ The heats of adsorption in the present case are, however, much smaller and so also is the proportionate decrease with change in surface concentration. Both these effects are manifestations of the fact that intermolecular forces are much smaller in molecular surface films than in atomic films.

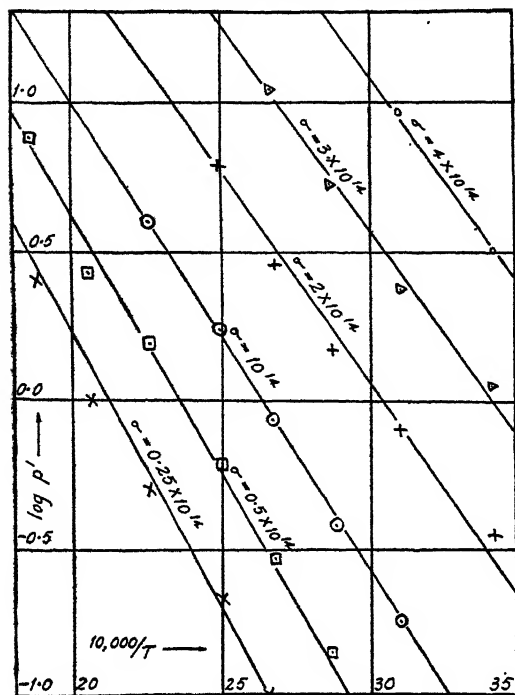


FIG. 3.

TABLE I.

$\sigma \times 10^{-14}$ Molecules per sq. cm.	E Calories per mole.
0.25	8300
0.5	7800
1	7300
2	6500
3	6200
4	6100

Summary.

The method of the maximum bubble pressure has been used to follow the changes in the surface tension of mercury produced by acetic acid vapour. The change has been followed at a number of temperatures from 20° C. to 260° C. The presence of the acetic acid vapour depresses both the surface tension and its temperature coefficient, and even results in a reversal of the sign of this last property over certain ranges of temperature. Calculations of the amount of acid adsorbed has been carried out. This amount decreases with temperature, so that the adsorption is accompanied by an evolution of heat. This heat of adsorption proves to be 6.1 kilocalories for close-packed films and rises to 8.3 kilocalories as the surface concentration is decreased to 0.25×10^{14} molecules per sq. cm.

⁶ R. C. L. Bosworth and E. K. Rideal, *Physica*, 1937, 4, 925.

A NOTE ON THE EFFECT OF CARBON DIOXIDE ON THE SURFACE TENSION OF MERCURY.

By R. C. L. BOSWORTH.

Received 12th June, 1939.

Measurements of the surface tension of mercury by the maximum bubble pressure method recently recorded by the author¹ has indicated that in the presence of CO_2 this property is only slightly less than its value in air. As past experiments had indicated strong selective adsorption of CO_2 by mercury,^{2, 3} and such adsorption is normally associated with a progressive lowering of the surface tension with increasing external pressure of the gas adsorbed it seemed desirable to examine the surface tension of mercury in the presence of air contaminated with various proportions of CO_2 .

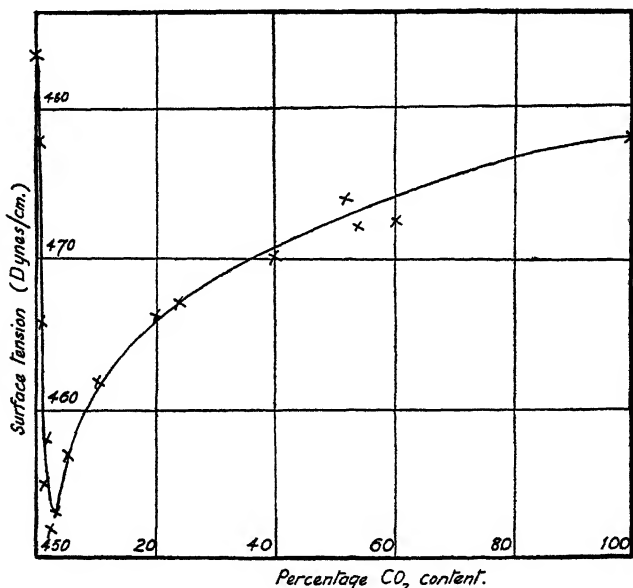


FIG. 1.

The CO_2 used in these experiments was prepared by igniting anhydrous lead carbonate, the gas was mixed with purified air and passed over P_2O_5 to remove any water vapour that might be present. A kathetometer recorded the amount of CO_2 present in the gas mixture passing into the vessel in which the surface tension was measured by the drop-weight method. These measurements are recorded in Fig. 1, which shows surface tension plotted against percentage composition of the air with respect to CO_2 .

It appears, then, that with increasing content of CO_2 the surface

¹ R. C. L. Bosworth, *Trans. Faraday Soc.*, 1938, 34, 1501.

² M. L. Oliphant, *Phil. Mag.*, 1928, 6, 422.

³ R. C. L. Bosworth, *Trans. Faraday Soc.*, 1932, 28, 896.

tension at first falls to a minimum some 8 % lower than the value in pure air, at about 3 % CO_2 , and thereafter rises very slowly with increasing CO_2 content, the value in pure CO_2 being about $1\frac{1}{2}$ % lower than the value obtained in pure air. Surface tension versus concentration curves of this same form have been recorded by Jones and Ray ⁴ in the case of electrolytes in aqueous solution, and McBain and Mills ⁵ have recently reviewed the literature connected with the occurrence of this type of curve. The present example appears to be of particular interest on account of the chemical simplicity of the substances involved, and the fact that we are here dealing with adsorption from the gaseous phase. As McBain and Mills would point out, strict application of the Gibbs Adsorption Equation to Fig. 1 would indicate strong positive adsorption of CO_2 below 3 % CO_2 content, zero adsorption at 3 % and negative adsorption at all higher values. These conclusions must be contrasted with the strong positive adsorption actually observed from all air- CO_2 mixtures, and would seem to indicate that the Gibbs layer on mercury is thick enough to contain oxygen (or nitrogen) in excess of the amount of CO_2 already found.

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⁴ G. Jones and W. A. Ray, *J. Amer. Chem. Soc.*, 1937, 59, 187.

⁵ J. W. McBain and G. F. Mills, *Physic. Soc. Reports*, 1938, 5, 30.

THE SURFACE TENSIONS OF TWO PHASE LIQUID SYSTEMS CONTAINING BENZENE.

By J. W. BELTON.

Received 20th June, 1939.

In a previous communication the writer recorded the surface tensions of some binary liquid mixtures containing benzene, and discussed the adsorption at the liquid-vapour interface.¹ This work has now been extended to systems in which two liquid phases are present. The adsorption of one component of a solution at the surface in contact with vapour may be calculated from surface tension and vapour pressure data; but if the solution is in contact with another liquid phase, adsorption will also occur at the liquid-liquid interface, and may be very different in extent from that at the liquid-vapour boundary. It is shown below that data regarding one interface may be valuable in calculating the adsorption at another, which otherwise would be very difficult to obtain.

Two such systems have been investigated—(1) benzene-carbon disulphide-water and (2) benzene-acetic acid-water—and these adsorptions calculated and compared. In the former the organic liquids are both immiscible with water, but completely miscible with each other; in the latter one component is soluble in both liquid layers.

Experimental.

The chemicals used were of analar grade, and were further purified until they gave a boiling-point or a freezing-point and a surface tension

¹ Belton, *Trans. Faraday Soc.*, 1935, 31, 1642.

of the accepted value. Solutions of varying concentration of benzene and carbon disulphide were made up by weight in stoppered bottles, and about an equal volume of water added. The bottles were sealed, and shaken in a thermostat at 25° C. for six hours, after which the layers were allowed to separate, when samples of each were taken. The surface tensions of these samples were measured at 25° C. by the bubble pressure method previously described by the writer.² The benzene-acetic acid-water systems were examined in the same way; the composition of the layers was found by weighing a sample and titrating with standard alkali.

1. Benzene-Carbon Disulphide-Water Systems.

The experimental results for this system are given in Table I. The interfacial tensions in the last column have been obtained from Antonow's Rule,³ *i.e.* that they are given by the difference between the surface tensions of the two phases; this rule is not invariably true, but its application here is justified by the results of Reynolds,⁴ who found that it held for many solutions against benzene. The surface tensions of the aqueous layers were found to be very little different from that of pure water. The surface tensions of the benzene-carbon disulphide layer give a smooth curve convex to the concentration axis when plotted against the molar percentage of benzene. The corresponding curve obtained from previously published data of the writer,¹ in the absence of a water layer, lies slightly below that when water is present, and joins it at the points representing the pure components.

TABLE I.

Moles % Benzene.	Moles % CS ₂ .	Aqueous Layer.		Benzene Layer.		γ_{12} .
		h .	γ_{2v} .	h .	γ_{1v} .	
—	100.00	11.62	72.10	5.46	31.41	40.69
17.40	82.60	11.60	71.98	4.835	29.98	42.00
35.75	64.25	11.61	72.05	4.715	29.23	42.82
51.00	49.00	11.58	71.86	4.60	28.53	43.33
74.18	25.82	11.60	71.98	4.56	28.28	43.70
100.00	—	11.60	71.98	4.54	28.16	43.82

The adsorptions at the liquid-liquid and the vapour-liquid interfaces may be calculated from the Gibbs equation; the method of calculation will, however, be clearer if the general case of a three component system in a vapour and two liquid phases is considered first. Let the components be A, B and C, the phases be represented by the subscripts v 1 and 2 respectively, μ be the chemical potential, and $\gamma_v \Gamma$ be the surface excess at the interface between the phases x and y . The Gibbs equation applied to the various interfaces then gives

$$d\gamma_{1v} = - {}_{1v}\Gamma_A d\mu_A - {}_{1v}\Gamma_B d\mu_B - {}_{1v}\Gamma_C d\mu_C \quad . \quad (1)$$

$$d\gamma_{2v} = - {}_{2v}\Gamma_A d\mu_A - {}_{2v}\Gamma_B d\mu_B - {}_{2v}\Gamma_C d\mu_C \quad . \quad (2)$$

$$d\gamma_{12} = - {}_{12}\Gamma_A d\mu_A - {}_{12}\Gamma_B d\mu_B - {}_{12}\Gamma_C d\mu_C \quad . \quad (3)$$

² Belton, *Trans. Faraday Soc.*, 1935, 31, 1413.

³ Antonow, *J. Chimie physique*, 1907, 5, 372; *Koll. Z.*, 1932, 59, 7.

⁴ Reynolds, *J. Chem. Soc.*, 1921, 114, 460.

Here the three components are considered to be present in all three phases; in certain special cases, however, these equations may be simplified.

(i) The components A and B are completely miscible with each other, but not miscible with C; that is the liquid phase 1 is composed of A and B, the liquid phase 2 of C only, and the vapour phase of A, B and C. At the liquid-vapour interface the term containing the insoluble vapour may be neglected (this is the usual procedure when a liquid phase containing two components is in contact with vapour which contains a slightly soluble third component such as air or nitrogen). The Gibbs equation then becomes

$$d\gamma_{1v} = - {}_1v\Gamma_A d\mu_A - {}_1v\Gamma_B d\mu_B \quad (4)$$

Similarly, as the third component, C, is absent from, or is present in only very small quantities in the liquid phase 2, the value of $d\mu_C$ becomes vanishingly small, and the Gibbs equation for the liquid-liquid interface may be written

$$d\gamma_{12} = - {}_{12}\Gamma_A d\mu_A - {}_{12}\Gamma_B d\mu_B \quad (5)$$

(ii) The component A is miscible with both B and C, but B is not miscible with C; that is the liquid phase 1 contains A and B, the liquid phase 2 contains A and C, and the vapour all three components. At the liquid-vapour interface the term involving the insoluble component may be neglected as above and we have

$$d\gamma_{1v} = - {}_1v\Gamma_A d\mu_A - {}_1v\Gamma_B d\mu_B \quad (6)$$

$$d\gamma_{2v} = - {}_2v\Gamma_A d\mu_A - {}_2v\Gamma_C d\mu_C \quad (7)$$

As component C is absent from, or is present in very small quantities in the liquid phase 1, and as component B is present only in very small quantities in liquid phase 2, for low concentrations of A, $d\mu_B$ and $d\mu_C$ will be small and we shall have

$$d\gamma_{12} = - {}_{12}\Gamma_A d\mu_A \quad (8)$$

The system benzene-carbon disulphide-water is an example of the special case (i); benzene and carbon disulphide are completely miscible with each other but not with water—the surface tensions of the liquid phases are very little different from those of water and of benzene-carbon disulphide mixtures. The various interfaces may therefore be treated as follows.

VAPOUR (v).		
		2
I		
CS ₂ (A)		
C ₆ H ₆ (B)		H ₂ O (C)

FIG. 1.

The system may be represented schematically by Fig. 1. The subscripts 1, 2, and *v* refer to the benzene-carbon

disulphide layer, the aqueous layer and the vapour phase respectively.

(a) The Liquid-Liquid Interface.

The Gibbs equation applied to this interface gives

$$d\gamma_{12} = - {}_{12}\Gamma_A d\mu_A - {}_{12}\Gamma_B d\mu_B \quad (9)$$

As the interfacial tension increases with benzene concentration, carbon disulphide will be adsorbed, and the dividing surface may be drawn so that $\Gamma_B = 0$. Hence

$$d\gamma_{12} = - {}_{12}\Gamma_A d\mu_A \quad (10)$$

(b) The Liquid-Vapour Interface.

The Gibbs equation for the benzene-carbon disulphide interface gives

$$d\gamma_{1v} = - {}_{1v}\Gamma_A d\mu_A - {}_{1v}\Gamma_B d\mu_B \quad (11)$$

Here the dividing surface may be drawn so that $\Gamma_A = 0$; hence

$$d\gamma_{1v} = - {}_{1v}\Gamma_B d\mu_B \quad (12)$$

This, combined with the Duhem-Margules equation

$$N_A d\mu_A + N_B d\mu_B = 0 \quad (13)$$

gives

$$d\gamma_{1v} = \frac{N_A}{N_B} {}_{1v}\Gamma_B d\mu_A \quad (14)$$

where N is the mole fraction.

Combining (10) and (14) we obtain

$$d\gamma_{12}/d\gamma_{1v} = - {}_{12}\Gamma_A N_B / {}_{1v}\Gamma_B N_A \quad (15)$$

According to Antonow's Rule

$$\gamma_{12} = \gamma_0 - \gamma_{1v} \quad (16)$$

where γ_0 is the surface tension of the aqueous layer; and if m is the benzene concentration

$$d\gamma_{12}/dm = - d\gamma_{1v}/dm \quad (17)$$

Hence from (15) and (17)

$${}_{12}\Gamma_A = \frac{N_A}{N_B} {}_{1v}\Gamma_B \quad (18)$$

${}_{1v}\Gamma_B$ may be calculated from vapour pressure data for benzene-carbon disulphide mixtures¹ and from $d\gamma_{1v}/dm$, which may be obtained from Table I; ${}_{12}\Gamma_A$ may then be calculated from equation (18). Adsorptions obtained in this way are given in Table II.

The adsorption of benzene at the liquid-vapour interface appears to rise to a maximum value and then falls, while that for carbon disulphide at the liquid-liquid interface falls as the benzene content increases. The value of ${}_{12}\Gamma_A \times 10^{10}$ of 2.95 moles/sq. cm. corresponds to an area of 55\AA^2 per molecule; there is thus ample room in the surface to accommodate the adsorbed molecules.

TABLE II.

Moles % Benzene.	${}_{1v}\Gamma_B \times 10^{10}$.	${}_{12}\Gamma_A \times 10^{10}$.
15	0.52	2.95
25	0.59	1.77
35	0.62	1.15
45	0.50	0.61
55	0.22	0.18
65	0.09	0.05
75	0.03	0.01
85	0.03	0.005

2. Benzene-Acetic Acid-Water Mixtures.

The experimental results for these systems are given in Table III, where the concentration of acetic acid is expressed in moles (m) per 1000 g. of solvent, and the interfacial tensions have been calculated from Antonow's Rule. If the surface tension of the aqueous layer is plotted against the concentration of acid in the same layer, a smooth curve is obtained, the surface tension at first falling rapidly and then more slowly; the curve for the surface tension of the benzene layer on the same diagram is almost horizontal. The two curves thus converge, and would

meet at that concentration at which the two layers disappear. This behaviour is due to the increasing solubility of benzene in the aqueous layer as the acid concentration increases. The surface tension of the aqueous layer, however, is the same as that of aqueous acetic acid solutions up to 16 M, above which the curves diverge, the effect of the dissolved benzene then becoming appreciable. The interfacial tension falls with increasing acid content, and the slope of the curve, plotted against benzene concentration in the aqueous layer, is almost equal to that for the vapour-aqueous layer interface. The plot of the surface tension of the benzene layer against the acid concentration in that layer does not, however, give a straight line; it falls sharply at first and then more slowly.

TABLE III.

Benzene Layer.		Aqueous Layer.		γ_{42}
m .	γ_{1v}	m .	γ_{2v}	
—	28.20	—	72.01	43.81
0.0183	28.18	0.726	61.65	33.77
0.0569	28.21	1.458	56.87	28.66
0.088	28.13	1.890	54.70	26.57
0.286	28.08	4.135	48.04	19.96
0.403	28.03	5.340	46.04	18.01
0.585	27.98	7.001	43.75	15.77
0.909	27.86	10.08	41.19	13.33
1.448	27.79	14.84	38.71	10.92
2.212	27.65	21.96	36.23	8.58
3.340	27.45	28.45	32.46	5.01
5.934	27.40	34.26	29.81	2.41
15.70	27.40	(one layer)		

The calculation of the adsorption at the interfaces is more difficult than in the case previously considered. At the lower concentrations very little benzene is present in the aqueous layer, and the vapour pressures of acetic acid in equilibrium with the system may be taken as equal to those of aqueous acetic acid solutions.

(a) The Benzene Layer-Vapour Interface.

The surface tension increments for this layer are very small and the corresponding vapour increments still smaller. It is therefore possible only to obtain very approximate values of $\Delta\gamma/\Delta\ln p$, and so also of the adsorption. It is shown below, however, that it is possible to calculate it indirectly from the adsorption at the liquid-liquid interface.

(b) The Aqueous Layer-Vapour Interface.

As acetic acid is adsorbed at this interface, the dividing surface may be drawn so that the surface excess of water is zero, and the Gibbs equation then gives

$$d\gamma_{2v} = - \frac{1}{2v} \Gamma_{HA} d_2 \mu_{HA} \quad . \quad . \quad . \quad (19)$$

Single acetic acid molecules have been chosen as a component. In the vapour phase, however, both single and double molecules exist in equilibrium, data for which at different temperatures have been obtained by

Wrewsky.⁵ The equilibrium constant at 25° C. may be calculated from the isochore, and from the total pressure of acetic acid the partial pressure of single molecules found. The adsorption in terms of single molecules may then be calculated from

$${}_{2v}\Gamma_{\text{HA}} = \Delta\gamma_{2v}/RT\Delta \ln p_{\text{HA}}. \quad (20)$$

The vapour pressures of dilute acetic acid solutions have been accurately measured by Fredenhagen and Liebster,⁶ whose data have been used to calculate the adsorption values given in Table IV. (The earlier calculation by the writer¹ for strong solutions did not consider this association.)

TABLE IV.

<i>m.</i>	${}_{2v}\Gamma_{\text{HA}} \times 10^{10}$	${}_{1v}\Gamma_{\text{HA}} \times 10^{14}$
0.075	0.64	0.09
0.15	1.08	0.18
0.25	1.64	0.32
0.4	2.23	0.57
0.6	2.64	0.84
0.9	3.07	1.18
1.3	3.41	1.78
1.5	3.68	2.21
1.7	4.09	2.45
1.9	4.49	2.70
2.1	4.69	2.82
2.3	4.24	3.18
2.5	4.01	3.44
2.7	3.52	3.52
2.9	3.28	3.94
3.1	3.5	4.16

(c) The Liquid-Liquid Interface.

The system, which may be schematically represented by Fig. 2, in which 1, 2 and B

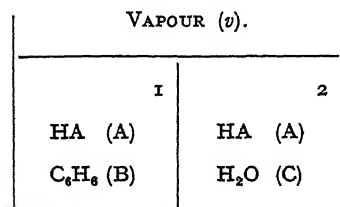


FIG. 2.

refer to the benzene layer, the aqueous layer and to benzene respectively, is an example of the second special case discussed on page 1356. It should be noted that the calculations have been restricted to solutions of fairly low acetic acid content, for which the surface tensions of the aqueous acetic acid layers are identical with those of aqueous acetic acid solutions of the same concentration. If the Gibbs equation is applied to the various interfaces we then obtain

$$(i) \quad d\gamma_{1v} = -{}_{1v}\Gamma_{\text{HA}} d_1\mu_{\text{HA}} - {}_{1v}\Gamma_{\text{B}} d_1\mu_{\text{B}} \quad (21)$$

$$\text{and if } {}_{1v}\Gamma_{\text{B}} = 0 \text{ then } d\gamma_{1v} = -{}_{1v}\Gamma_{\text{HA}} d_1\mu_{\text{HA}} \quad (22)$$

$$(ii) \quad d\gamma_{2v} = -{}_{2v}\Gamma_{\text{HA}} d_2\mu_{\text{HA}} - {}_{2v}\Gamma_{\text{B}} d_2\mu_{\text{B}} \quad (23)$$

$$\text{and if } {}_{2v}\Gamma_{\text{B}} = 0 \text{ then } d\gamma_{2v} = -{}_{2v}\Gamma_{\text{HA}} d_2\mu_{\text{HA}} \quad (24)$$

$$(iii) \quad d\gamma_{12} = -{}_{12}\Gamma_{\text{HA}} d_1\mu_{\text{HA}} \quad (25)$$

At equilibrium

$${}_{1\mu}\text{HA} = {}_{2\mu}\text{HA} = {}_{v\mu}\text{HA} \quad (26)$$

and hence

$$\left. \begin{aligned} d\gamma_{1v} &= -{}_{1v}\Gamma_{\text{HA}} d_v\mu_{\text{HA}} \\ d\gamma_{2v} &= -{}_{2v}\Gamma_{\text{HA}} d_v\mu_{\text{HA}} \\ d\gamma_{12} &= -{}_{12}\Gamma_{\text{HA}} d_v\mu_{\text{HA}} \end{aligned} \right\} \quad (27)$$

⁵ Wrewsky, *Z. physik. Chem.*, 1928, 137, 362.

⁶ Fredenhagen and Liebster, *ibid.*, A, 1932, 162, 449.

Further

$${}_{1v}\Gamma_{HA} = {}_{2v}\Gamma_{HA} \frac{d\gamma_{1v}}{d\gamma_{2v}} \quad . \quad . \quad . \quad . \quad (28)$$

and

$${}_{12}\Gamma_{HA} = {}_{2v}\Gamma_{HA} \frac{d\gamma_{12}}{d\gamma_{2v}} \quad . \quad . \quad . \quad . \quad (29)$$

The adsorption at the aqueous layer-vapour interface may be obtained by the method given under (b); the other adsorptions can then be calculated from the surface tension data.

From Antonow's Rule we obtain

$$\frac{d\gamma_{12}}{dm} = \frac{d\gamma_{2v}}{dm} - \frac{d\gamma_{1v}}{dm} \quad . \quad . \quad . \quad . \quad (30)$$

where m is the concentration of acetic acid in the aqueous layer. $d\gamma_{1v}/dm$ may be neglected compared with $d\gamma_{2v}/dm$ and hence

$${}_{12}\Gamma_{HA} \approx {}_{2v}\Gamma_{HA} \quad . \quad . \quad . \quad . \quad (31)$$

The adsorption at the liquid-liquid interface is thus almost the same as that at the aqueous layer-vapour interface (actually it will be just a little greater).

The values of the adsorptions at the various interfaces calculated in this way are given in Table IV. There is a surface excess of acetic acid at each interface of the system; that between the two liquid layers and that between the aqueous layer and the vapour passes through a maximum at a concentration of acetic acid in the aqueous layer of 2 M; that between the benzene layer and the vapour increases throughout the concentration range considered. The corresponding area per molecule at the maximum is 35\AA^2 , which represents a fairly closely packed film; the area corresponding to a concentration of 0.15 M is 154\AA^2 . The area per molecule at the benzene-vapour interface is much greater, $1.6 \times 10^5\text{\AA}^2$ for 0.15 M and $5.6 \times 10^3\text{\AA}^2$ for 2.2 M.

It is of interest to compare these results with those of Harkins and McLaughlin,⁷ who concluded for benzene-acetic acid-water systems that the area per molecule at the aqueous layer-benzene interface is 23 per cent. less than at the interface between water and air. According to the results described above there is very little difference between these values, the presence of benzene as the upper layer producing only a slight effect on the number of molecules adsorbed; this adsorption thus appears to be dependent on the dimensions of the acetic acid molecules in the film. This agrees with the results of Harkins and King⁸ for butyric acid, which is adsorbed to the same extent at the interfaces between water and benzene, water and hexane and water and air.

Summary.

The surface tensions of the liquid phases of the systems (a) benzene-carbon disulphide-water, (b) benzene-acetic acid-water have been measured. The Gibbs equation is applied to the data, and the relation-

⁷ Harkins and McLaughlin, *J. Amer. Chem. Soc.*, 1925, 47, 1610.

⁸ Harkins and King, *ibid.*, 1919, 41, 970.

ship between the amount of solute adsorbed at the liquid-vapour and liquid-liquid interfaces is discussed. It is shown that the adsorption of acetic acid at the aqueous phase-vapour interface may be calculated by an indirect method, and that it is almost equal to that at the liquid-liquid interface.

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THE SURFACE REACTION BETWEEN OXONIUM IONS AND MICA.

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It is well known that some salts, notably ammonium iodide, crystallise in a regular way on freshly cleaved mica. The crystals appear as tetrahedra (Fig. 1) regularly arranged, instead of as randomly arranged cubes, the normal arrangement on an indifferent surface such as glass. It was found, after a few qualitative trials to discover whether this process could be influenced, that immersion in $N-H_2SO_4$ for a short time, followed by washing, completely destroyed the regular arrangement of ammonium iodide crystallised from solution. Alkali, however, had no influence, even when the mica was boiled for half an hour with $10\ N-KOH$; treatment for the same time at room temperature by saturated solutions of KCl , $CaCl_2$ and $BaCl_2$, which were chosen for their neutrality, likewise had no influence on the orienting power.

These experiments suggested that with sufficiently dilute acid the reaction velocity could be studied by observing the gradual change of crystal pattern from complete to zero orientation. Convenient reaction times were found in the range of $pH\ 2.5-6$.

Experimental.

The mica was of good quality and was split immediately before the experiment. It retained its power to orient crystals of ammonium iodide over the duration of the experiment, so that grease from the air did not affect the results. The pH of the ammonium iodide was too high for the mica surface to be attacked by this solution. The mica was held by forceps at the corners only, and only interior laminae were selected. Buffer solutions of citric acid and disodium hydrogen phosphate, as used by McIlvaine¹ in the presence of a trace of fungicide, were maintained at a constant temperature of 25° , and small strips of mica were plunged into the medium for times noted on a stop-watch. The mica was quickly withdrawn, plunged into concentrated KOH to check the reaction, washed with distilled water and drained on filter paper. The upper side of the mica, which did not touch the paper, was used for the crystallisation. After draining, the mica was placed on a warm metal surface and a drop of dilute ammonium iodide allowed to dry up slowly on the mica. The film of crystals was then examined microscopically and the

¹ McIlvaine, *J. Biol. Chem.*, 1921, 49, 183.

number of cubic and tetrahedral crystals in the field was counted, using an eyepiece graticule; in some instances counting was done on photographic plates. The percentage of tetrahedral crystals was obtained as the mean of a number of counts, duplicate runs being made in almost every case. An untreated mica surface invariably gave 100 per cent. of oriented crystals.

The values of the pH were checked by means of a glass electrode in the Department of Leather Technology, and were constant over long periods.

TABLE I.

Time in secs.	% Tetrahedral Crystals.	log %.
6	100	2.00
24	95	1.978
48	84.4	1.926
73	80.0	1.903
120	59.2	1.772
180	51.8	1.714
240	44.3	1.646
360	30.9	1.490

Stirring was effected by means of a stream of CO_2 -free air during some of the runs at high pH , but no influence of the agitation could be detected.

There were slight variations in reaction velocity on raising the temperature to 45° ; however, these could be explained by the slight change of pH of the buffer with temperature, so that the energy of activation must be zero or at the most a few thousand calories per g. mol.

The progressive increase in disorientation is shown in the micro-photographs, Figs. 1-4.

Some of the cubic crystals appear as prisms owing to the internal structure due to growth being revealed.

The percentage of tetrahedral crystals decreased with time according to an exponential law, as is seen in the typical result for pH 4.74.

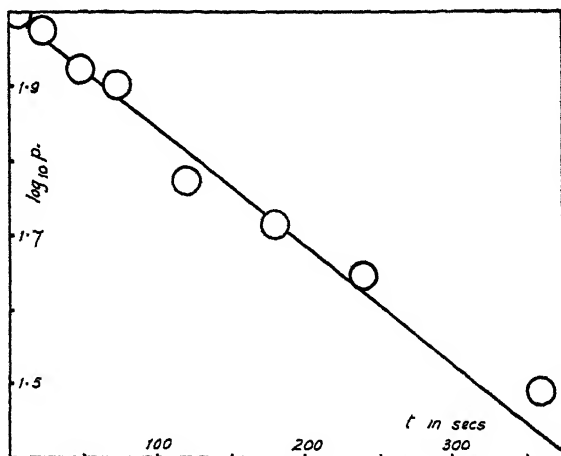


FIG. 5.

These results are plotted on Fig. 5. The $\log p - t$ curve (where p is the per cent. of tetrahedral crystals) is linear, *i.e.*,

$$p = p_0 e^{-kt} = 100 e^{-kt} \quad (1)$$

The velocity coefficient is very dependent on pH , as can be seen from Table II. $\log k$ when plotted against pH gave an approximately straight line.

$$\log_{10} k = 0.91 - 0.76 pH \quad (2)$$

Actually a slight curvature is shown by the points, amounting to deviations from the line of app. $\pm 0.1 \text{ } \mu\text{H}$.

Discussion.

The structure of muscovite was determined by Pauling and Jackson and West.² The structure consists of a firmly bound double sheet made up of two hexagonal networks of linked silicon-oxygen tetrahedral groups united by Al atoms, the double sheet being separated from one another by a hexagonally arranged plane of K ions. It is probably across the latter plane that the mica cleaves, and it is probable that the K ions evenly distribute themselves on the two surfaces formed by cleavage.³

The spacing between the K ions is 5.2 Å, which is very near the value of the edge of the smallest tetrahedron which can be cut from an ammonium iodide cube, *viz.*, 5.14 Å. The crystal nucleus is therefore able to fit with very little distortion on to the mica pattern, giving tetrahedra regularly arranged.

When the mica is split and then placed in a solution of ammonium iodide it is probable that the negative points of the surface become rapidly covered by adsorbed ammonium ions, which will act as nuclei for crystallisation with the same efficacy as the potassium ions already on the surface. This explains why no cubic crystals grow on the surface, even although the surface in air must contain patches bare of potassium ions. The precise nature of the nucleation process remains a mystery, which would require a knowledge of migration frequencies and energy levels of the potassium ions on the surface as well as a knowledge of kinetics in concentrated strong electrolytes. All lattice points will be treated as equivalent, which will cause no error, as percentages, not absolute numbers, of crystals are considered.

The events supposed to occur in ammonium iodide will be repeated when the mica is plunged into the buffer solutions. In so far as the concentration of sodium ions greatly exceeds that of oxonium ions the former will be preferentially adsorbed. This will certainly be a rapid process for a unimolecular layer involving times negligible compared with those employed, which were of the order of 1-30 minutes. It is probable that the cause for the slowness of the reaction is to be sought in some explanation other than that of adsorption. A probable explanation lies in the replacement of potassium or sodium ions by oxonium ions, *i.e.* a slow exchange reaction. In support of this it is known that concentrated HCl attacks mica, giving a solution of KCl.⁴ Diffusion is unlikely to be a controlling factor since removal of oxonium ions is made good by further dissociation of buffer, and in fact stirring did not influence the rate. At first sight it might be thought that the

TABLE II.

μH .	h .	$-\log_{10} h$.
2.60	6.5×10^{-2}	1.187
3.02	4.5×10^{-2}	1.347
3.56	2.1×10^{-2}	1.679
3.85	1.3×10^{-2}	1.886
4.74	1.5×10^{-3}	2.824

² Pauling, *Proc. Nat. Acad. Sci.*, 1930, 16, 123; *cf.* also W. L. Bragg, *The atomic structure of minerals*, 1937; Jackson and West, *Z. Krist.*, 1930, 76, 211; 1933, 85, 160.

³ Armbruster and Austin, *J.A.C.S.*, 1938, 60, 467.

oxonium ions would be as effective for crystallisation as the very similar potassium ions. It is, however, very inexact to treat the charge of the oxonium ions as concentrated at the centre, just as for water itself the treatment of the structure as a dipole is inexact⁵ (e.g., Bernal and Fowler regard the attachment of a water molecule to a negative ion as occurring through one proton, so that the dipole axis is not directed towards the centre of the ion). The union of an oxonium ion with a negative point on the surface will likewise occur by the attachment of a proton, and thus the charge of the latter will be screened off by the rest of the oxonium ion from the region of the solution. It is possible, however, that the proton attached to the negative region of oxygen atoms becomes attached to the latter, giving OH groups (of which two already exist in the structure) so that the proton is assimilated by the mica. In this way it is possible to give an explanation of the inertness of the surface as regards orientation.

Let there be n_0 potassium ions per cm^2 of the cleavage plane of the mica before splitting, and n after immersion in buffer for time t , i.e. $n_0 - n$ lattice points have been replaced by oxonium ions.

$$\text{Then} \quad \frac{dn}{dt} = -k_1 n, \quad . \quad . \quad . \quad (3)$$

where k_1 is a constant dependent on the rate of replacement of metallic by oxonium ions.

$$\text{Hence} \quad n = n_0 e^{-k_1 t}. \quad . \quad . \quad . \quad (4)$$

If the number of crystallisation nuclei which give oriented crystals is identified with n , then p , the percentage of oriented to total crystals, is given by

$$p = 100 n/n_0 = 100 e^{-k_1 t}, \quad . \quad . \quad . \quad (6)$$

i.e. a logarithmic decay is obtained, as observed.

The photographs for unattacked mica show that the orientation of the ammonium iodide crystals is almost perfect in one direction and hence the orienting power of the mica cannot be due to the K atoms alone, which would give tetrahedra in equal numbers pointing in opposite directions. Hence the silicate backing must be operative as well, for this is such that the structures on opposite sides of the K plane are mirror images of one another. It should be remembered that it is probable that on cleavage the K atoms sink to some extent into the structure below. The net effect is that approximately half the possible orientations are missing. The action of the oxonium ion on the silicate structure mentioned above fits in with this view, and it is possible that some colloidal silicic acid is formed.

It is interesting to observe the progressive appearance of the opposite orientation as the surface is etched by acid. Presumably the opposite orientation is due to patches on the surface stepped down one or an odd number of double sheets from the surface plane, and these regions would be less exposed to attack, so that the ratio of the number of crystals with the second orientation to that with the first would increase.

It is probable that three contiguous cations arranged as an equilateral triangle are necessary for the formation of a crystal nucleus

⁴ J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VI, p. 618.

⁵ Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

giving a tetrahedral crystal of ammonium iodide. The crude theory above therefore needs refining. The number of equilateral triangles on the mica surface per cm^2 giving one type of orientation is n_0 . Let the number of these "destroyed" as nucleation centres by replacement of one or more cations by oxonium ions be y . Then

$$p = \left(\frac{n_0 - y}{n_0} \right) 100. \quad (7)$$

In order to study how y changed with n , 100 points were numbered off consecutively 1-100 to form a hexagonal array in the form of a square; 100 cards numbered consecutively 1-100 were thoroughly shuffled and the numbers of consecutive cards in the pack were then recorded. As each number turned up the corresponding point on the paper was marked. This represented a reaction. The number of triangles "destroyed" was counted. At first every lattice point marked implied the destruction of three triangles, but as the surface filled up the number of triangles destroyed per point decreased, owing to the fact that a triangle was regarded as destroyed when only one of its apices was marked, so that the marking of a second or third apex did not contribute to y . Allowance was made for the edges, which are negligible in the case of the mica surface. It was found that except for the final portion of the curve

$$-dy/dn = k_2 n + k_3 \quad (8)$$

$$\text{or} \quad -y = \frac{1}{2} k_2 n^2 + k_3 n - \frac{1}{2} k_2 n_0^2 - k_3 n_0, \quad (9)$$

since $n = n_0$ when $y = 0$.

Hence, from equation 7,

$$\frac{1}{2} k_2 n^2 + k_3 n + (n_0 - \frac{1}{2} k_2 n_0^2 - k_3 n_0 - n_0 p / 100) = 0,$$

$$\text{giving} \quad n = -k_3 + \sqrt{k_3^2 - 2k_2 z} / k_2,$$

$$\text{where} \quad z = n_0 - \frac{1}{2} k_2 n_0^2 - k_3 n_0 - n_0 p / 100. \quad (10)$$

The other root does not agree with the condition that

$$k_2 n + k_3 = \text{positive}.$$

Now from equation (7) $dp/dy = -100/n_0$ and from equation (3) and equation (8)

$$\frac{dp}{dt} = \frac{dy}{dn} \cdot \frac{dn}{dt} \cdot \frac{dp}{dy} = -\frac{100}{n_0} k_1 n (k_2 n + k_3). \quad (11)$$

$$\text{Hence} \quad \frac{dp}{dt} = -A(-k_3 + \sqrt{C + Dp})\sqrt{C + Dp}, \quad (12)$$

where $A = 100k_1/(n_0 k_2)$;

$$C = k_3^2 - 2k_2(n_0 - \frac{1}{2} k_2 n_0^2 - k_3 n_0) \quad \text{and} \quad D = 2 \frac{n_0}{100} k_2.$$

Hence $\log(-k_3 + x) = -k_1 t + \text{const.}$, where $x = \sqrt{C + Dp}$,

when $p = 100$, $t = 0$ and $x = k_3 + k_2 n_0$.

$$\text{Hence} \quad \log \left(\frac{x - k_3}{k_2 n_0} \right) = -k_1 t.$$

Now $k_3 + k_2n_0 = 3$ and $k_3 = -1.2$ from the experiment with cards. Hence, finally,

$$\log \left(\frac{\sqrt{0.6 + 0.084p} + 1.2}{4.2} \right) = -k_1 t, \quad (13)$$

which gives the correct initial but not final conditions. It is found that $\log (\sqrt{0.6 + 0.084p} + 1.2)$ when plotted against t gives straight lines for which the following values (Table III) of k_1 may be inferred:—

TABLE III.

$pH.$	$k_1.$	$-\log_{10} k_1.$
2.6	1.58×10^{-2}	1.801
3.02	1.13×10^{-2}	1.947
3.56	5.2×10^{-3}	2.284
3.85	3.63×10^{-3}	2.440
4.74	4.8×10^{-4}	3.189

When $\log k_1$ is plotted against pH an approximate straight line is obtained, given by

$$\log k_1 = 0.17 - 0.72 pH,$$

which is the amended version of equation (2). The fact that $k_1 = k_0[H^+]^{0.72}$ is perhaps significant in suggesting that the reaction

velocity is controlled by the surface concentration of oxonium ion, which may be written $[H^+]^{\frac{1}{2}}$ if adsorption is neglected, rather than by the bulk concentration as on the classical collision theory.

It is hoped to correlate the attack of the mica surface by means of acid solutions with the adsorption of gases on the surface after reaction in solution.

Summary.

Sheets of freshly cleaved mica immersed for short times in solutions of low hydrogen ion concentration do not give the complete orientation of crystals of ammonium iodide obtained with unattacked mica, but give a mixture of oriented tetrahedra and unoriented cubes, the proportion of the latter increasing with time of immersion in the acid solution. The results are interpreted in terms of surface attack by oxonium ions.

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INFRA-RED ABSORPTION SPECTRA OF AsH_3 , AsD_3 AND PD_3 .

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The investigation of these molecules was undertaken with a view to obtaining data from which their dimensions might be calculated. Previous workers had reported low dispersion results for AsH_3 ¹ and PD_3 .²

We have now examined the low dispersion spectra of AsD_3 and PD_3 and have also obtained high dispersion plots of certain bands in all three molecules. We are therefore able to contribute (a) a more

¹ Robertson and Fox, *P.R.S., A.*, 1928, 120, 128.

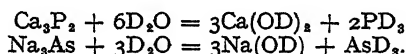
² Sutherland and Conn, *Nature*, 1936, 138, 641.

accurate knowledge of the vibration frequencies of PD_3 , (b) the corresponding frequencies for AsD_3 and (c) the value of I_A for AsH_3 .

With a view to obtaining I_A accurately for the light and heavy compounds it was at first decided to investigate the fine structure of the bands corresponding to ν_1 in the three molecules. The AsH_3 ν_1 absorption was successfully resolved, but the PD_3 and AsD_3 bands fall in a region of intense atmospheric absorption due to water vapour which makes accurate work impossible and the attempts were abandoned. Instead, efforts were made to resolve the weak overtone bands due to $2\nu_1$ falling near 3300 cm^{-1} for PD_3 and 3020 cm^{-1} for AsD_3 . In the case of PD_3 , the very low intensity of the overtone was not sufficient for an absorption plot to be made, while the AsD_3 overtone was very complex and an accurate value of I_A could not be obtained from it. Owing to difficulties of this nature, and to the fact that the ratio of the moments of inertia of the H and D compounds is not sensitive to changes in the value of the apex angle, it became more important to determine the values of the four fundamental frequencies from which it was found possible to deduce the dimensions of the molecules with fair accuracy.

Experimental.

The arsine used was a sample supplied to us by Dr. H. J. Emeléus. The heavy arsine and phosphine were prepared using the following reactions:—



The heavy water had an estimated D content of 99 %. The calcium phosphide was a B.D.H. product and the sodium arsenide was prepared *in situ* by heating metallic sodium and arsenic. Initial degassing of the reactants to eliminate light hydrogen was achieved by heating the phosphide and arsenide to about 450°C . *in vacuo* and by repeated freezing and melting of the heavy water, also *in vacuo*. The products of the reaction were separated from higher deuterium phosphides or arsenides by repeated evaporation from a CO_2 -acetone bath. The presence of about 3 % of the light compounds was inferred by observing the intensity of the fundamental ν_1 .

The prism instrument for the low dispersion work was of the standard Hilger type D83 used in conjunction with a sensitive moving magnet galvanometer. Fluorite, sylvine, and rock salt prisms were used and the slit widths employed are shown in the diagrams. Only those regions of the spectrum were plotted where absorption due to the D compounds was expected to lie. The high dispersion spectra were plotted with a grating instrument which is described elsewhere.³ Gratings of 7200, 4800, and 1200 lines per inch were used and slit widths were of the order of 1 cm^{-1} . With both instruments a stationary absorption cell was used, connected directly to the gas reservoir, with a mercury manometer and a liquid air trap for controlling the pressure. This stationary all-glass system was very convenient to manipulate and was also necessary because the gases were poisonous and had to be kept free from traces of air. The path length of the beam through the cell was 24 cm.

Results.

The new data obtained are included in Table I. NH_3 and ND_3 frequencies are included also for comparison in connection with the next paper (page 1376).

³ Sutherland, Lee and Conn, (*to be published shortly*).

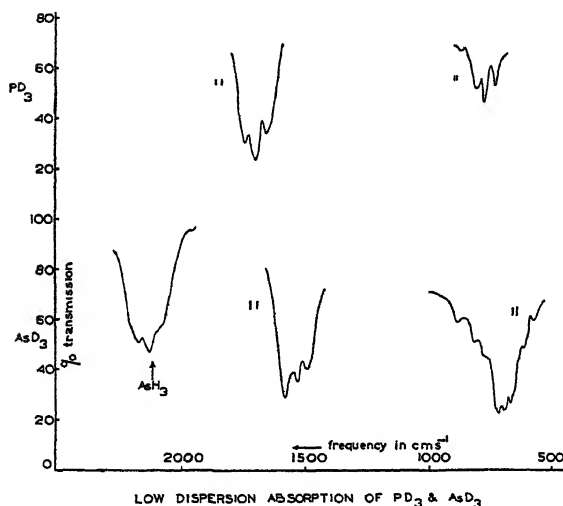
TABLE I.

	PH ₃ .	PD ₃ .	AsH ₃ .	AsD ₃	NH ₃ .	ND ₃ .
ν_1	2327	1694	2122	1534	3335	2420
ν_2	2421	—	2185	—	3415*	2556
ν_3	992.4	730	906	660	933	749.2
	990.0				966	745.8
ν_4	1121.4	806	1005	714	1631	1191.3
$I_A \times 10^{40}$	6.22	—	7.43	—	2.82	5.397

* The value 3415 cm.⁻¹ for ν_2 in ammonia comes from Barker's analysis of the absorption at 4 μ . It may be that this value is a little low. (Cf. Sutherland, *Physic. Rev.*, 56, in print.)

(a) Low Dispersion Spectra of AsD₃ and PD₃.

Low dispersion transmission curves for AsD₃ and PD₃ are shown in Fig. 1. The absorption in the AsD₃ curve at 2120 cm.⁻¹ was obtained



LOW DISPERSION ABSORPTION OF PD₃ & AsD₃

FIG. 1.

when attempts were made to find a combination tone in this region with a relatively high pressure of 30 cm. of the gas. The fact that this band falls exactly in the position corresponding to the strong absorption of the AsH₃ fundamental shows that it is almost certainly due to the presence of a few per cent. of the light compound. The band found in PD₃ by Sutherland and Conn² at 2325 cm.⁻¹ and attributed by them to a combination frequency $\nu_1 + \nu_2$ is very probably also due to the PH₃ impurity present, as its position agrees exactly with the ν_1 absorption of this molecule. The bands at 1694 cm.⁻¹ and 1534 cm.⁻¹ for PD₃ and AsD₃ respectively were obtained using gas pressures of 3½ cm., and correspond to the fundamental ν_1 . They both show the characteristic three-branch structure of a parallel band, though the resolution is rather poor, as wide slits are necessary in this region. The absorption in the region of 800 cm.⁻¹ for PD₃ and 700 cm.⁻¹ for AsD₃, corresponding to the low frequency vibrations ν_3 and ν_4 showed in each case three main maxima. At first sight they appear to correspond to the P, Q, and R branches of a single band but the high resolution work of Fung and Barker⁴ has shown that in PH₃ there are at least two vibrations absorbing here. The low resolution of the prism instrument was not sufficient to allow the three peaks to be identified.

⁴ Fung and Barker, *Physic. Rev.*, 1934, 45, 238.

(b) High Dispersion.

Fig. 2 shows a transmission curve obtained for PD_3 near 750 cm^{-1} with slit widths of 1 cm^{-1} and a pressure of 10 cm. of gas in the cell. No attempt was made to make a complete and accurate plot of the absorption in this band. We had two objects in view: (1) to determine the nature of the three peaks found under low dispersion, and hence to obtain values of the frequencies ν_3 and ν_4 , and (2) to see if there was any Q branch doubling similar to that found by Fung and Barker in the corresponding band of PH_3 . It is seen at once that the two outer peaks at 730 cm^{-1} and 806 cm^{-1} correspond to

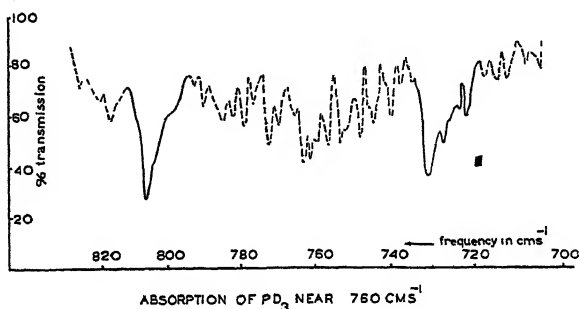


FIG. 2.

Q branches of the two bands ν_3 and ν_4 respectively, and that the central peak of the low dispersion curve is due to overlapping of the accompanying fine structure. The close similarity between the spectra of PH_3 and AsH_3 shown by the work of Robertson and Fox¹ leads to the conclusion that the corresponding three peaks of AsD_3 of the low dispersion curve can be interpreted in a similar way. Thus the frequencies identified by Howard⁵ with the vibrations ν_1 , ν_3 and ν_4 have now been determined for

TABLE II.—WAVE NUMBERS OF LINES IN THE 4.7μ BAND OF AsH_3 .

1	2261.1	22	2173.3	43	2104.9	64	2045.8
2	2254.5	23	2170.2	44	2100.6	65	2043.5
3	2248.9	24	2166.5	45	2097.8	66	2040.4
4	2245.1	25	2163.1	46	2093.0	67	2037.7
5	2242.0	26	2159.2	47	2090.3	68	2034.4
6	2238.8	27	2156.5	48	2085.2	69	2032.3
7	2235.7	28	2152.5	49	2082.7	70	2029.3
8	2229.8	29	2149.0	50	2077.3	71	2027.5
9	2226.0	30	2145.2	51	2075.6	72	2024.5
10	2223.2	31	2141.7	52	2073.4	73	2021.3
11	2216.6	32	2137.8	53	2072.2	74	2018.3
12	2210.9	33	2133.6	54	2069.4	75	2016.2
13	2203.7	34	2131.2	55	2068.3	76	2012.7
14	2199.2	35	~ 2126	56	2065.0	77	2008.5
15	2197.1	36	2123.1	57	2061.7	78	2008.0
16	2192.8	37	2122.3	58	2059.6	79	2004.2
17	2190.5	38	2121.1	59	2056.9	80	2001.3
18	2186.5	39	2117.6	60	2054.0	81	1999.5
19	2183.7	40	2116.4	61	2052.5	82	1997.9
20	2179.8	41	2115.2	62	2051.2	83	1995.9
21	2176.8	42	2108.4	63	2049.0		

all four molecules. With regard to the possible doubling of the ν_3 Q branch it can be stated that, within the limits set by the resolution of the instrument and the width of the peak, the latter is single. A doublet separation of 1 cm^{-1} could have been detected.

The absorption in the 2120 cm^{-1} region of AsH_3 due to 24 cm. of gas at $3\frac{1}{2}\text{ cm.}$ pressure is indicated in Fig. 3. The slits used included 1 cm^{-1} .

⁵ Howard, *J. Chem. Physics*, 1935, 3, 208.

There is a strong *Q* branch, sharp on the high frequency edge, and accompanied by *P* and *R* branches, each possessing a structure much more complex than that of a simple parallel band. The wave numbers of the

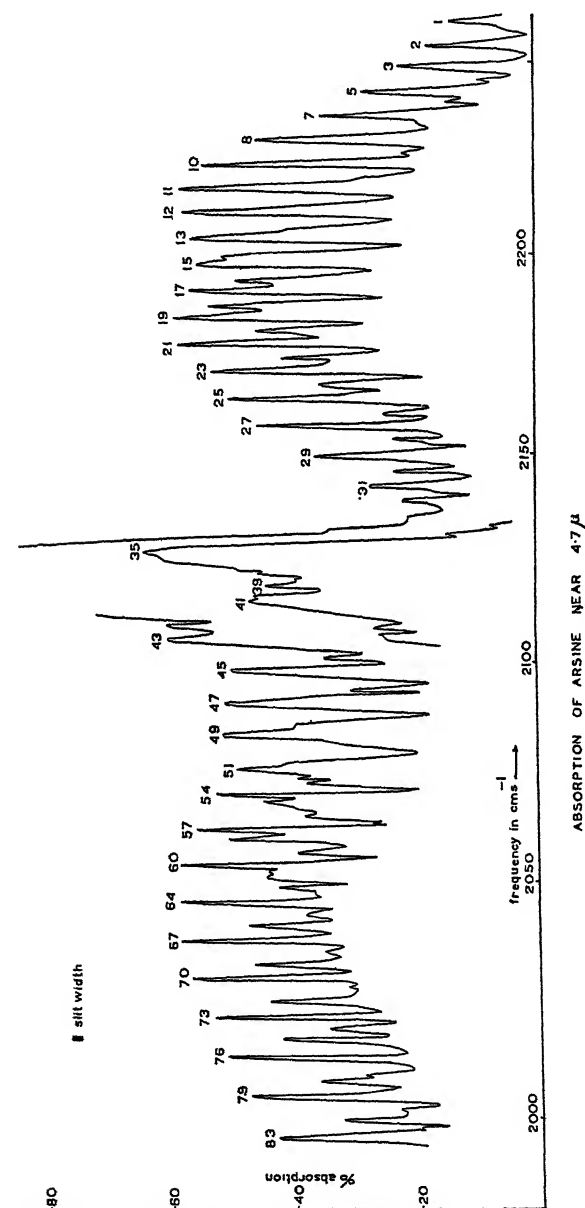


FIG. 3.

lines are given in Table II. From the rotation line spacing a moment of inertia $I_A = 7.43 \pm .03 \times 10^{-40}$ g. cm.² is deduced. Certain interesting aspects of this band are discussed later.

Discussion.

Assignment of Frequencies.

Recent attempts to assign the absorption bands of PH_3 to fundamental vibrations have been made by Fung and Barker,⁴ while Howard⁵ considered NH_3 , ND_3 , AsH_3 , and PH_3 . The latter, by substituting the values assigned to ν_1 and ν_4 , and probable values for the apex angle, in equations developed by Lechner⁸ on the basis of the valency force field, evaluated the force constants of the molecules. Those force constants were then used to calculate the frequencies ν_2 and ν_3 . The agreement with the observed frequency was found to be good in the case of ν_3 , while ν_2 was computed to fall very near ν_1 (see Table I). A test, both of this assignment of the frequencies, and of the applicability of the valency force field, is furnished by using the force constants obtained for PH_3 and AsH_3 to calculate all four frequencies for PD_3 and AsD_3 . The results together with the observed values for comparison are given in Table III. The agreement is usually within 3 %, showing that Howard's assignment of the absorption bands is correct, and that the valency force field gives a good approximation to the actual force distribution. An important result is that in all cases the calculated value of ν_2 is within 2 % of the observed value for ν_1 .

TABLE III.—FUNDAMENTAL FREQUENCIES OF PD_3 AND AsD_3 .

	PD_3				AsD_3			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
Calculated from valency force field	1665	1681	762	798	1490	1512	674	716
Observed in infra-red (gas)	1694	—	730	806	1534	—	660	714
Observed ⁶ in Raman (liq.)	1664	—	748	805	—	—	—	—

Fung and Barker's assignment of ν_1 , ν_3 and ν_4 in PH_3 is in agreement with the later one of Howard, but in order to explain the presence of a double Q branch at 990 cm^{-1} , one being due to ν_3 , they attributed the other to ν_2 . Howard, on the other hand, offers no explanation of this double peak. The possibility that the assignment is wrong, and that the 990 doublet is due to the splitting of the degenerate ν_4 vibrations, is discounted by the success of Howard's assignment. The only other obvious explanation is that the doubling of ν_3 is due to the passage of the phosphorus atom through the plane of the hydrogen atoms. This will be discussed in the next paper.

The 2120 cm^{-1} band of AsH_3 .

Of the four molecules AsH_3 , AsD_3 , PH_3 and PD_3 the absorptions due to the fundamental parallel vibration ν_1 for all but the first lie in regions of the spectrum which are difficult to investigate under high resolution. It is important, therefore, to study carefully the band due to AsH_3 , which is free from this trouble. The band (Fig. 3) con-

⁶ De Hemptinne and Delfosse, *Bull. Sci. Acad. Roy. Belg.*, 1935, **21**, 793.

sists of a strong central Q branch sharp on the high frequency edge and flanked by P and R branches which show structure much more complex than that of a simple parallel band, probably due to the overlapping of ν_1 and ν_2 . The main characteristics of the complex structure are as follows:—

(1) The absorption in the low frequency side near the Q branch is very much stronger than the corresponding region in the positive branch.

(2) The strong lines 83, 79, 76, . . . , do not continue to the same zero as the strong lines 1, 2, 3, . . . 15, 17, 19 In other words, no numbering of these lines can be furnished such that a line is obtained which passes through the origin on graphing $\nu_n - \nu_{-n}$ against n .

(3) The extra lines in the region 83–64 and 35–1 are not irregular but seem to occupy positions definitely related to the position of the stronger regularly placed lines which can almost certainly be associated with ν_1 .

It is interesting to compare this band with the corresponding absorption of PH_3^4 , ND_3^7 and NH_3^8 . The great similarity between the vibration spectra of AsH_3 and PH_3 would lead to the probability of the similarity extending to the rotational structure also. This is what is found when the 4.3μ band of PH_3 is examined. Even though the resolution is poor it can be observed that the lines are very complex. There is strong absorption on the low frequency side of the Q branch. Also, if the line numbering and frequency values of Fung and Barker are used an effect similar to (2) in AsH_3 is found. No effect of this nature is found in NH_3 and ND_3 . In each case there is a complex structure, more pronounced in the positive branch, which is explained⁸ as due to the simple overlapping of the parallel band ν_1 and the perpendicular band ν_2 . In the case of NH_3 , however, the Q branch spacing which has to be given to ν_2 in order to explain the band structure is very different from that predicted by Johnston and Dennison.⁹

It is very probable that the structure of these bands is complicated by interaction between the rotation levels of ν_1 and ν_2 due to Coriolis terms in the Hamiltonian which couple them. This type of perturbation has been described by Jahn.¹⁰ The terms arise because of the Coriolis forces set up when the molecule is rotating perpendicular to the figure axis which tend to convert the parallel vibrations into perpendicular vibrations. According to Dr. Jahn* the perturbation may impart parallel type activity to ν_2 and may split the levels of ν_1 . Whether the line structure obtained can be entirely explained by these interactions or not, can only be decided when the necessary calculations are made.

Summary.

The infra red absorption spectra of gaseous AsD_3 , PD_3 , and AsH_3 have been studied with a view to obtaining data from which their molecular structure might be calculated. By comparing calculated and ob-

⁷ Migeotte and Barker, *Physic. Rev.*, 1936, 50, 418.

⁸ Barker, *ibid.*, 1939, 55, 657.

⁹ Johnston and Dennison, *ibid.*, 1935, 48, 868.

¹⁰ Jahn, *Physic. Rev.* 1939, 56, 680.

* The authors would like to thank Dr. Jahn for information on this subject.

served values of the absorption frequencies it is shown that the valency force field gives a good representation of the actual intramolecular forces. The 4.7μ ν_1 fundamental band of AsH_3 has been plotted and a value of 7.43×10^{-40} g. cm.² is deduced for I_A . The rotation structure of this band is complex, probably due to overlapping of ν_2 and interaction between the rotation levels of ν_1 and ν_2 .

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THE DIMENSIONS OF THE PHOSPHINE AND ARSINE MOLECULES AND THE POSSIBILITY OF OPTICALLY ACTIVE DERIVATIVES.

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Ever since the investigations of Dennison Hardy and Uhlenbeck¹ established the dimensions of ammonia and proved that the easy passage of the nitrogen atom through the plane of the hydrogens precludes the possibility of optically active derivatives, it has been a matter of considerable interest to know whether the same holds true for phosphine and arsine. Qualitatively the effect of such a phenomenon is to produce a doubling of all the lines in the "parallel" absorption bands of the vibration-rotation spectrum. Dennison and Uhlenbeck have shown the magnitude of the splitting of each energy level (which gives rise to the doubling) depends only on the dimensions of the molecule and on the magnitude of the vibration frequency involved, while later authors² have made more detailed calculations on how the exact height of the potential barrier is related to the observed splittings. The starting point of all those methods is an implicit or explicit assumption of the dimensions of the molecule and we shall accordingly consider first the determination of the dimensions of phosphine and arsine from the spectroscopic data now available.

We take for granted the pyramidal model with the hydrogens at the corners of an equilateral base. The two moments of inertia $I_A (= I_B)$ and I_C (about the symmetry axis) are then given in terms of the height h , and of β the angle between the altitude and any bond by the formulæ

$$\left. \begin{aligned} I_A = I_B &= \left(\frac{3M}{3m + M} + \frac{3}{2} \tan^2 \beta \right) mh^2 \\ I_C &= 3 \tan^2 \beta mh^2 \end{aligned} \right\} \quad (1)$$

where m is the mass of a hydrogen atom. The spacing between the rotational lines of the parallel bands gives I_A directly, but the determination of I_C is more complicated. In principle the method is to determine spacings of the Q branches in the two perpendicular fundamental vibration rotation bands. Unfortunately these spacings are not yet available from

¹ Dennison and Hardy, *Physic. Rev.*, 1932, 39, 938; Dennison and Uhlenbeck, *ibid.*, 1932, 41, 313.

² Manning, *J. Chem. Physics*, 1935, 3, 136; Morse and Rosen, *Physic. Rev.*, 1932, 42, 210.

the spectra and are probably so small that they would not lead to very accurate results in any case. We are left, then, with a relation between h and β established by our knowledge of I_A and must seek other means of determining either β or h .

The most obvious method is to examine the parallel bands in spectra of PD_3 and AsD_3 . This method has, however, two very serious drawbacks. The first is that the band corresponding to ν_1 is in each case in a very awkward region of the spectrum, *viz.* 6μ , where irregular absorption due to water vapour makes the determination of a line structure extremely difficult, while the band corresponding to ν_3 is in each case complicated by being overlapped by ν_4 . These points have already been brought out in the preceding paper. The second objection is more fundamental, and lies in the fact that the ratio of the spacing in the deuterium substituted molecule to that in the ordinary molecule is not very sensitive to a change in the angle of the molecule. Thus from equation (1) we have

$$\frac{I_A^H}{I_D} = \frac{m_H \left(\frac{\tan^2 \beta}{2} + \frac{M}{3m_H + M} \right)}{m_D \left(\frac{\tan^2 \beta}{2} + \frac{M}{3m_D + M} \right)} \quad (2)$$

in which M is the mass of the apical atom and the suffixes H and D refer to hydrogen and deuterium. It is clear that unless β is very small the $\tan^2 \beta$ term will be the dominating term in the bracket and the ratio of the moments of inertia is hardly distinguishable from m_H/m_D . Consequently when we rewrite (2) as an equation for β we get an expression in which both numerator and denominator are hardly different from zero. The value for β so obtained will clearly be very unreliable unless the spacings can be determined with a degree of precision not yet attainable in infra-red spectroscopy.

We are therefore forced to consider methods of determining β purely from a knowledge of the vibration frequencies. At first sight this may seem a hazardous procedure in view of the known weakness of this method for triatomic molecules.³ It appears, however, that the same objections do not apply to the group molecules NH_3 , PH_3 and AsH_3 . The principle of this method is to assume a particular force field for the intramolecular motions and from the resulting equations which connect the frequencies, the atomic masses, the force constants and the dimensions, to eliminate the unknown force constants, leaving one or more relations between the frequencies, masses and dimensions. It is to be remembered that for PH_3 and AsH_3 we have a fairly accurate knowledge of all four fundamental frequencies and for PD_3 and AsD_3 we know ν_1 , ν_3 and ν_4 but not ν_2 . The possibility of using the most general potential function of the second degree⁴ can therefore be considered. Such a function contains six potential constants, and since we have seven observed frequencies, it should be possible to determine the unknown angle β . The reason this procedure has not been followed is that with the present data the equations are not self-consistent. This is due to neglect of the anharmonic corrections and until these are known the use of such an elaborate method is unjustified. Moreover, there would be no check on the value of β , since all the data had been used to determine it. We

³ Penney and Sutherland, *P.R.S.*, 1936, 156, 654.

⁴ Rosenthal, *Physic. Rev.*, 1935, 47, 235.

have preferred, therefore, to use a simpler force field, the well-known valency force field, which only involves two force constants and determine β independently from the hydrogen and the deuterium compounds.

The equations which follow from the assumption of a valency force field in this type of molecule were first given by Lechner,⁵ and are reproduced below:—

$$n_1^2 n_3^2 = \frac{f}{m} \frac{6d}{m} p \frac{2 \cos^2 \beta}{1 + 3 \cos^2 \beta} \quad . \quad . \quad . \quad (3)$$

$$n_1^2 + n_3^2 = \frac{f}{m} \left[1 + (p - 1) \cos^2 \beta \right] + \frac{6d}{m} \frac{2 \cos^2 \beta}{1 + 3 \cos^2 \beta} (p - (p - 1) \cos^2 \beta) \quad (4)$$

$$4n_2^2 n_4^2 = \frac{f}{m} \frac{6d}{m} \frac{2}{1 + 3 \cos^2 \beta} \left[p + (2 - p) \cos^2 \beta \right] \quad . \quad . \quad (5)$$

$$2(n_2^2 + n_4^2) = \frac{f}{m} \left(1 + p - (p - 1) \cos^2 \beta \right) + \frac{6d}{m} \frac{1 + \cos^2 \beta}{1 + 3 \cos^2 \beta} \left(1 + \frac{1}{2} (p - 1) \frac{(1 - \cos^2 \beta)^2}{1 + \cos^2 \beta} \right) \quad (6)$$

where $p = \frac{M + 3m}{M}$, f is the valency force constant along a bond, d is the angle force constant for deformation, and $n_1 = 2\pi\nu_1$, etc.

We notice immediately that

$$\frac{n_1^2 n_3^2}{n_2^2 n_4^2} = \frac{\nu_1^2 \nu_3^2}{\nu_2^2 \nu_4^2} = \frac{4p \cos^2 \beta}{p + (2 - p) \cos^2 \beta} \quad . \quad . \quad (7)$$

giving β directly in terms of the four fundamentals.

Although there are sufficient data to solve the equation for β in the case of PH_3 and AsH_3 , our ignorance of ν_2 prevents its direct employment for PD_3 and AsD_3 . However, by making the assumption that $\frac{\nu_1}{\nu_2} \sim 1$ (see previous paper) we get the approximate relation

$$\frac{\nu_3^2}{\nu_4^2} = \frac{4p \cos^2 \beta}{p + (2 - p) \cos^2 \beta} \quad . \quad . \quad . \quad (8)$$

which can be employed for the deuterium compounds. The results of applying both (7) and (8) to the data in Table I of the previous paper are shown in Table I. In this table we have given α instead of β where α is the angle between any two PH or AsH bonds. The relation between α and β is:—

$$\sin \beta = \frac{2}{\sqrt{3}} \sin \frac{\alpha}{2} \quad . \quad . \quad . \quad (9)$$

It will be noticed that for phosphine and arsine the three values of α obtained do not differ by more than 2° and there is equally good agreement between the four values of α obtained for ammonia. The average of the latter (111°) differs from the value of α obtained by Migeotte and Barker⁶ from a comparison of the rotational fine structures in NH_3 and ND_3 by approximately 3° . This is an extremely encouraging result and

⁵ Lechner, *Sitz. ber. Akad. Wiss., Wien*, 1932, 141, 633.

⁶ Migeotte and Barker, *Physic. Rev.*, 1936, 50, 418.

we can be fairly sure that the values for α obtained for phosphine and arsine are correct to within this error. Additional confirmation may be sought in several different ways. The values of β may be used in (4) and (5) to determine f and d and substitution of f , d and β in (3) or (6) should then be a test of the consistency of the valency force field and so of the method. On applying this test it was found that the agreement between the two sides of (3) was exact to the fourth significant figure, while the two sides of (6) agreed to within 4 per cent. In this connection

TABLE I.

	Phosphine.		Arsine.		Ammonia.		
	From PH ₃ .	From PD ₃ .	From AsH ₃ .	From AsD ₃ .	From NH ₃ .	From ND ₃ .	From Rotational Structure.
α from (7) .	100° 30'	—	98° 30'	—	112°	111°	108° 24'
α from (8) .	99°	98° 30'	97° 30'	96°	111° 30'	110° 30'	—
β from row 1	62° 30'	—	61°	—	73° 30'	72°	69° 15'
h . .	0.67	—	0.75	—	.30	—	.36
I_A/I_G .	0.77	0.74	0.81	0.80	0.64	0.60	.62 .60
XH . .	1.46	—	1.56	—	1.026	—	1.016
From Badger .	1.43	—	1.54	—	1.00	—	1.00
Covalent Radii * .	1.40	—	1.51	—	1.00	—	1.00

* The values for the covalent radii of the atoms have been taken from Pauling, *Nature of the Chemical Bond*, Cornell University Press (1939), using 0.30 Å as a mean value for the hydrogen radius. All distances in the table are given in terms of Ångström units.

it is worth remarking that an attempt to carry out the test evaluating f and α from (4) and (6) and then substituting in (3) and (5) yielded extremely poor results. The reason for this is that (4) and (6) are extremely bad equations to use for evaluating d and any error in d is magnified greatly when employed in the product terms of (3) and (5).

A less satisfactory but rather interesting test is to see how well the relation

$$\frac{(\nu_1^2 \nu_3^2)^H}{(\nu_1^2 \nu_3^2)^D} = \frac{\rho_H m_D^2}{\rho_D m_H^2} \quad . \quad . \quad . \quad (10)$$

is fulfilled. This relation is derived from (3), but it also holds for the most general field of the second degree. The agreement obtained therefore is rather a test of the error due to the neglect of anharmonicity. The results of the test are shown in Table II, and indicate that anharmonic corrections are more serious in ammonia than in either of the other two. This is very satisfactory.

Again, one may evaluate the PH and AsH distances and compare

them with those obtained by using Badger's relation,⁷ and the values of the PH and AsH force constants given by Howard.⁸ The result of such a comparison is shown in Table I, and is again entirely in agreement. This last, however, is not a very sensitive test.

Having obtained reasonably accurate values for the dimensions of the phosphine and arsine molecules, we next investigate the nature of the potential barrier restricting the passage of the P and As atoms through the plane of the hydrogens. The wave mechanical solution of this problem was first given by Dennison and Uhlenbeck,¹ who represented the potential barrier by means of two parabolas joined by a straight line (Fig. 1). Other treatments have been given² employing more complicated representations for the potential curve, but the difference in the results obtained is not very significant. We shall employ the equations of Dennison and Uhlenbeck, as these are most convenient for computation. According to these authors the splittings in the ground state $\Delta\nu_0$, and in the first vibrational state $\Delta\nu$ of ν_3 are given by the equations

$$\frac{\Delta\nu_0}{\nu_1} = \frac{2\alpha}{\sqrt{\pi}} \exp. (-\alpha^2 - 2(x_0 - \alpha)\sqrt{\alpha^2 - 1}) \quad (11)$$

$$\frac{\Delta\nu}{\nu} = \frac{4\alpha(\alpha^2 - 1)}{\sqrt{\pi}} \exp. (-\alpha^2 - 2(x_0 - \alpha)\sqrt{\alpha^2 - 3}) \quad (12)$$

where
$$x_0 = \left(\frac{h}{4\pi^2\mu\nu}\right)^{-\frac{1}{2}} h_0, \quad \mu = \frac{3mM}{M+3m},$$

h is Planck's constant, and the interpretation of α is clear from Fig. 1.

Knowing the height h_0 , we can evaluate α if we know the splitting in one of the levels, and the height of the barrier then follows from the relation

$$V = \alpha^2 h\nu/2.$$

The experimental data so far give only one example of a splitting which might be due to a cause of this kind, *viz.* in the ν_3 band of phosphine, the Q branch of which is double with a separation of 2.4 cm^{-1} . The pure rotation spectrum of PH_3 showed no observable splitting,⁹ which means that Δ_0 must be less than 0.4 cm^{-1} . Since the splitting in ν_3 measured by $\Delta_0 + \Delta_1$, we may assume as a first approximation that Δ_0 is negligible, and take $\Delta_0 = 2.4 \text{ cm}^{-1}$. This leads to a value for

α of 1.83 and for V of 1655 cm^{-1} . Using this value of α , we calculate

⁷ Badger, *J. Chem. Physics*, 1934, 2, 128; and 1935, 3, 710.

⁸ Howard, *ibid.*, 1935, 3, 207.

⁹ Wright and Randall, *Physic. Rev.*, 1933, 44, 391.

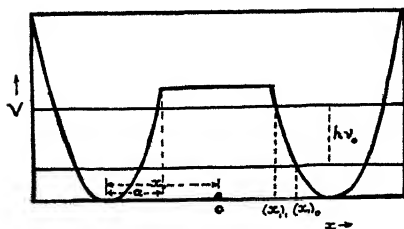


FIG. 1.

Δ_0 to be $1.51 \times 10^{-4} \text{ cm.}^{-1}$, so justifying our original approximation. The value of Δ_1 for ν_1 will be of the same order as Δ_0 , so that a measurable splitting in ν_3 is quite consistent with an immeasurably small splitting in ν_1 and in the pure rotation spectrum.

In an attempt to get confirmation of a more positive character, we next computed the separation Δ_1 to be expected for the ν_3 band of PD_3 on the assumption that V was the same in PH_3 and PD_3 . We obtained a value of $6.81 \times 10^{-4} \text{ cm.}^{-1}$. Since all other splittings would have been considerably smaller, we did not trouble to calculate them. The fact that no splitting has been observed in for PD_3 is again consistent with these calculations. The value obtained for V is slightly lower than that found by Dennison and Uhlenbeck for ammonia, *viz.* 1770 cm.^{-1} . The latter, however, differs a little from the value given by Manning,² and by Morse and Rosen,² of just over 2000 cm.^{-1} , so it may be that Dennison and Uhlenbeck's method has given a slightly low value for the height of the barrier in phosphine.

TABLE III.

	PH_3	PD_3	AsH_3	AsD_3
x_0	6.05	7.04	6.62	7.75
α	1.83	2.13	1.98	2.32
Δ_0	1.51×10^{-4}	1.84×10^{-7}	5.33×10^{-6}	1.093×10^{-9}
Δ_1	2.4 *	6.81×10^{-4}	3.3×10^{-2}	3.98×10^{-6}
V	1655	1655 *	1655 *	1655 *

* Indicates that this value was assumed as a basis for the calculations: the units in the last three rows are all cm.^{-1} .

Finally, seeing the value of V for PH_3 came out to be within 6 per cent. of that for NH_3 , we calculated the splitting Δ_1 to be expected in the ν_3 bands of AsH_3 and AsD_3 , on the assumption that V has the same value there. The results in Table III show that the separations in the bands would be quite unobservable. Again, the experimental evidence is in agreement so far as it goes, but very little work has been done on the arsines using high resolving power. The fact that nearly all these splittings are too small to be observed in vibration rotation or pure rotation spectra makes one consider the possibility of observing them directly in the ground state in the way employed by Cleeton and Williams¹⁰ for ammonia. Corresponding to the ammonia band found by them at a wave-length of 1.5 cm. , phosphine might be expected to show absorption of wireless waves of about 60 m. wave-length. It should be remembered, however, that the intensity of absorption, being roughly proportional to the square of the frequency, will be only about 5×10^{-8} of what it was in ammonia. The practical difficulties of detecting such an absorption are very obvious.

Finally, we might remark briefly on the application of the above results to the problem of optical activity. It is interesting to note that although the frequency of inversion of both phosphine and arsine mole-

¹⁰ Cleeton and Williams, *Physic. Rev.*, 1934, **45**, 234.

cules appears to be extremely high, it is decreasing steadily from PH_3 (about $5 \times 10^6/\text{sec.}$) to AsD (about 30 per second). The effect of substituting D for H is particularly noteworthy. In both PH_3 and PD_3 this reduces the frequency of inversion by a factor of about 1000. The results in Table III also demonstrate that provided the height of the potential barrier preventing inversion remains the same, then increasing the length of the bond (*i.e.* the height of the pyramid) has a very drastic effect in reducing the frequency. This suggests that the substitution of large groups in place of the hydrogens might well produce a molecule for which the frequency of inversion is sufficiently slow to enable optically active isomers to be separated at low temperatures.

We wish to thank Miss D. M. Simpson for help with the computations involved in the above work, Dr. N. Nath for discussion, and Professor D. M. Dennison, who pointed out the excessive weakness of the absorption which might be expected from phosphine at 60 metres. A grant from the Chemical Society for certain materials is gratefully acknowledged.

Summary.

A determination of the dimensions of the phosphine and arsine molecules has been made from the spectroscopic data available on PH_3 , PD_3 , AsH_3 , AsD_3 . Since complete analysis of the rotational structure of the bands is not yet possible, it has been necessary to use the assumption of a valency force field to determine the apical angle from purely vibrational data. Various cross checks with the better known case of ammonia indicate that the method gives results which are not likely to be out by more than 3 per cent. The dimensions obtained are:—

	XH Bond.	XHX Angle.	Height of Pyramid.
Phosphine	1.46 Å	99°	0.67 Å
Arsine	1.56 Å	97°	0.75 Å

These dimensions are next employed in calculating the height of the barrier restricting the passage of the phosphorus atom through the plane of the hydrogens, which is practically the same as in ammonia, *viz.* about 2000 cm.^{-1} . The frequency of inversion is, however, roughly 1000 times less than in ammonia. Further calculations indicate that the substitution of large massive groups for the hydrogens may well give a molecule for which the frequency of inversion would be sufficiently slow to permit the separation of optically active isomers at sufficiently low temperatures.

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THE THERMODYNAMICS OF ACID-BASE EQUILIBRIA.

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1. Introduction.

From the early days of the Ionic Theory the electrolytic dissociation of acids has excited interest partly because acids form the greater portion of the class of weak electrolytes which obey the Ostwald Dilution Law, and partly because the extent of their dissociation clearly depends upon their chemical structure. The problem of the relation between structure and ionisation has retained its interest, but it has become obvious that any exact study of this relationship must comprise also a consideration of the effects of solvent and temperature upon ionisation.

The examination of the ionisation of acids from the standpoint of the Law of Mass Action was first put on an exact modern basis by Bjerrum¹ and Brönsted,² whose work, combined with the important technical advances of MacInnes and Shedlovsky,³ and of Harned and Owen,⁴ has made possible the precise determination of acid strength. Mainly from the work of Harned and his collaborators we now have accurate results for the dissociation constants of many acids at various temperatures: it is our object in this paper to analyse critically these and some other data for acid dissociation, and to give a summary of the values of the thermodynamical functions obtained from our analysis.

We believe that the results of our analysis are as accurate as the data permit, but it must be remembered that experiments on equilibria in solution are necessarily restricted by the range of existence of the liquid state: the most precise data for acid dissociation in water cover the range 0°-60°, some less precise results extend to 100°, and a very few go up to 300°. To a certain extent the restriction of the temperature range is compensated by the accuracy of at least some of the results, but it is possible that the interpolation formulæ which we have employed lose their significance when used over a much wider range of temperature than that actually investigated.

2. Analysis of Experimental Data.

In carrying out the analysis of the data, we have taken the thermodynamic equations

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad . \quad . \quad . \quad (1)$$

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad . \quad . \quad . \quad (2)$$

¹ Bjerrum, *Z. Electrochem.*, 1918, 24, 321.

² Brönsted, *J. Chem. Soc.*, 1921, 119, 574.

³ MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, 1932, 54, 1429.

⁴ Harned and Owen, *ibid.*, 1930, 52, 5079.

and made the simplifying assumption that ΔC_p is independent of the temperature, thereby arriving at the equation

$$\ln K = A/T + \frac{\Delta C_p}{R} \ln T + B \quad (3)$$

This equation has also been used by Pitzer,⁵ who showed that with a value of $\Delta C_p = -40$ cal./deg. a better representation of the data for the fatty acids is obtained than with Harned and Embree's⁶ empirical equation

$$\log K - \log K_m = p(t - \theta)^2 \quad (4)$$

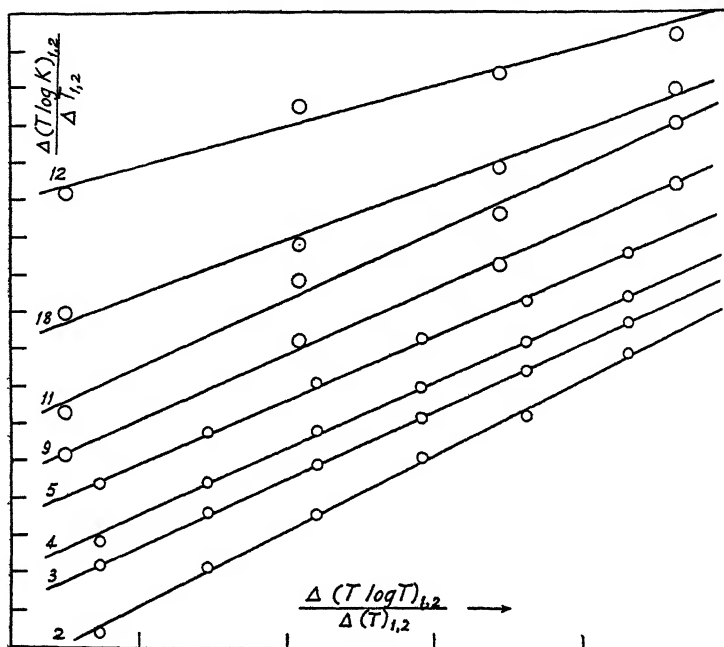


FIG. 1.

$$\frac{\Delta(T \log K)_{1,2}}{\Delta T_{1,2}} \quad v. \quad \frac{\Delta(T \log T)_{1,2}}{\Delta T_{1,2}}$$

- | | |
|---------------|------------------------------|
| 2. Formic. | 9. Benzoic. |
| 3. Acetic | 11. <i>m</i> -Nitro-benzoic. |
| 4. Propionic. | 12. <i>o</i> -Iodo-benzoic. |
| 5. Butyric. | 18. <i>o</i> -Toluic. |

Since ΔC_p is regarded as independent of temperature, we may write the equations

$$\Delta H = \Delta H_0 + \Delta C_p T \quad (5)$$

$$\Delta S^0 = \Delta S_0^0 + \Delta C_p \ln T \quad (6)$$

Dividing (5) by T and subtracting (6), we get

$$\Delta G^0/T = \Delta H_0/T - \Delta C_p \ln T + (\Delta C_p - \Delta S_0^0) \quad (7)$$

whence,

$$\ln K = -\Delta H_0/RT + \frac{\Delta C_p}{R} \ln T + (\Delta S_0^0 - \Delta C_p)/R \quad (8)$$

⁵ Pitzer, *J. Am. Chem. Soc.*, 1937, **59**, 2365.

⁶ Harned and Embree, *ibid.*, 1934, **56**, 1050.

and we see that the constants A and B of equation (3) have the significance

$$A = \Delta H_0/R.$$

$$B = (\Delta S_0^0 - \Delta C_p)/R.$$

By rearrangement of equation (3) we obtain for two temperatures, T_1 and T_2 ,

$$T_1 \log K_1 = A' + \frac{\Delta C_p}{R} T_1 \log T_1 + B' T_1,$$

$$T_2 \log K_2 = A' + \frac{\Delta C_p}{R} T_2 \log T_2 + B' T_2,$$

whence on subtraction

$$\frac{T_1 \log K_1 - T_2 \log K_2}{T_1 - T_2} = \frac{\Delta C_p}{R} \cdot \frac{T_1 \log T_1 - T_2 \log T_2}{T_1 - T_2} + B',$$

or

$$\frac{\Delta_{1,2}(T \log K)}{\Delta_{1,2}(T)} = \frac{\Delta C_p}{R} \cdot \frac{\Delta_{1,2}(T \log T)}{\Delta_{1,2}(T)} + B' \quad (9)$$

The slope of the straight line obtained by plotting

$$\frac{\Delta_{1,2}(T \log K)}{\Delta_{1,2}(T)} \quad \text{against} \quad \frac{\Delta_{1,2}(T \log T)}{\Delta_{1,2}(T)}$$

for a set of values of T_1 and T_2 gives $\Delta C_p/R$ and hence ΔC_p .

The linearity of these curves, shown in Fig. 1, is strong evidence for the validity of the assumption that ΔC_p is constant over the range of temperature employed. A change of 2 cal./degree over the whole range would produce a noticeable curvature.

From equation (3) we see that if $(\log K - \frac{\Delta C_p}{R} \log T)$ is plotted against $1/T$, straight lines should be obtained, and using our values of ΔC_p we have the lines shown in Fig. 2. The slope of each of these lines is $A' = -\Delta H_0/2 \cdot 303 R$.

From the values of ΔH_0 and ΔC_p , we can calculate the temperature at which $\Delta H = 0$ for any particular acid. This temperature, T_m , is given by

$$T_m = \frac{-\Delta H_0}{\Delta C_p} \quad (10)$$

Values of T_m may also be obtained by graphical interpolation from the plots of $\log K$ against temperature, since from equation (1) T_m is the temperature corresponding to the stationary value of $\log K$. The agreement between the results of the two methods of evaluating T_m is to within one or two degrees, and shows both the consistency of the data and the accuracy with which our equation represents them.

The results of the above analysis applied to the available data are given in Table I. This also includes the values of $\Delta G_{298.1}^0$ calculated from $\log K_{298.1}$; of $\Delta H_{298.1}$ obtained from

$$\Delta H_T - \Delta H_0 = \Delta C_p T,$$

and of $\Delta S_{298.1}^0$ evaluated from

$$\Delta S_{298.1}^0 = \frac{\Delta H_{298.1} - \Delta G_{298.1}^0}{298.1}$$

The sixth and seventh columns give the values of A and B which, on substitution in equation (3) together with the appropriate value of ΔC_p , yield the equation which we consider to give the best representation of the experimental data. Values of ΔH_0 have not been tabulated since they may be calculated readily from A . This quantity is quite sensitive

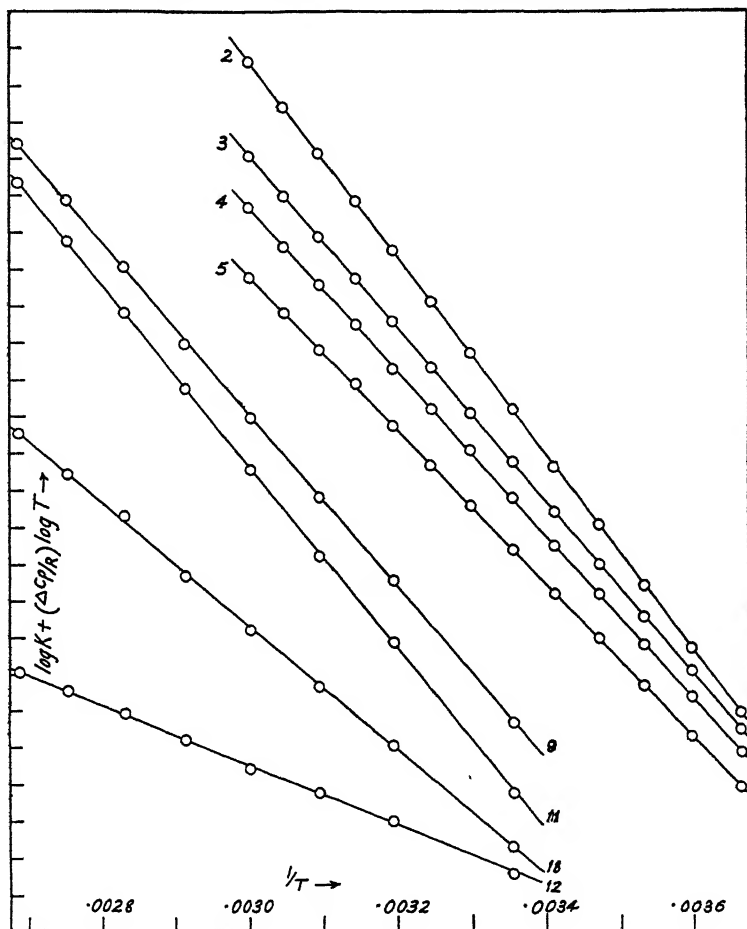


FIG. 2.

$$\log K + \frac{\Delta C_p}{R} \log T \quad \text{v.} \quad \frac{1}{T}$$

- | | |
|---------------|------------------------------|
| 2. Formic. | 9. Benzoic. |
| 3. Acetic. | 11. <i>m</i> -Nitro-benzoic. |
| 4. Propionic. | 12. <i>o</i> -Iodo-benzoic. |
| 5. Butyric. | 18. <i>o</i> -Toluic. |

to small changes in ΔC_p so that values of ΔH_0 calculated from it are probably only reliable to about ± 200 cal. In the range of experimental measurements, however, ΔH is probably reliable to ± 50 cal.

The results of Harned and his collaborators have not always been expressed in the same form, and their extrapolation methods have undergone progressive change. We have therefore re-examined their

TABLE I.*—VALUES OF THE THERMODYNAMIC FUNCTIONS† FOR THE DISSOCIATION OF ACIDS.†

Acid.	$+ \Delta C_p$ (cal./deg.).	$+ \Delta S_{298-1}^0$ (cal./deg.).	ΔG_{298-1}^0 (cal.).	ΔH_{298-1} (cal.).	-A.	B.	T_m °K.
1 Water	-51.0	-18.9	19122	13490	6274.0	70.4940	564.0
2 Formic	-41.4	-17.3	5114	— 40	2684.1	56.7186	297.0
3 Acetic	-36.6	-22.1	6483	— 100	2358.9	47.6856	295.3
4 Propionic	-35.4	-22.9	6644	— 170	2265.9	46.7696	293.2
5 Butyric	-34.6	-24.4	6570	— 700	2098.0	45.2729	278.0
6 Chloroacetic	-39.0	-16.9	3898	-1150	2286.4	53.3068	268.7
7 Lactic	-40.2	-18.2	5259	— 174	2578.0	54.7716	294.0
8 Glycollic	-40.2	-17.2	5222	100	2660.0	55.0749	302.0
9 Benzoic	-36.2	-18.9	5682	40	2362.6	48.7922	300.0
10 o-NO ₂ -Benzoic	-23.7	-21.3	2980	-3355	809.0	30.2255	156.5
11 m-NO ₂ -Benzoic	-37.2	-14.7	4703	320	2492.0	50.9329	307.0
12 o-I-Benzoic	-21.9	-24.0	3903	-3250	823.0	27.1195	173.0
13 m-I-Benzoic	-37.0	-17.0	5260	190	2447.4	50.3641	303.0
14 o-Cl-Benzoic	-28.3	-21.5	3926	-2470	1302.8	36.6278	211.0
15 Salicylic	-47.7	-10.2	4055	1000	3327.8	67.5734	320.0
16 m-OH-Benzoic	-29.9	-18.1	5561	170	1980.0	39.6774	303.0
17 Anisic	-49.7	-17.8	6110	800	3405.0	68.7824	314.0
18 o-Toluic	-30.6	-22.4	5284	-1400	1683.5	39.8765	252.0
19 m-Toluic	-32.6	-19.2	5785	70	2135.0	43.4995	300.0
20 p-Toluic	-36.6	-18.9	5923	300	2444.9	49.3876	306.0
21 Cinnamic	-35.8	-18.1	6009	600	2469.6	48.4156	314.8
22 α-Br-Cinnamic	-29.0	-19.1	2698	-2990	1233.0	38.2935	194.0
First Acid Dissociation of Amino-Acids.							
23 Glycine	-33.8	-7.3	3304	1100	2455	47.9494	333
24 Alanine (i)	-33.4	-8.2	3190	750	2332	47.0521	320
24 Alanine (ii)	-41.0	-8.1	3201	800	2830	58.1174	317
25 α-NH ₂ -n-Butyric	-44.2	-9.2	3116	370	2950	62.5409	306
26 α-NH ₂ -n-Valeric	-32.6	-8.9	3160	510	2232	42.7490	314
27 Norleucine	-32.6	-8.9	3183	530	2235	45.7421	314
28 α-NH ₂ -iso-butyric	-38.6	-9.1	3220	900	2620	54.4346	311
29 Valine	-38.6	-10.3	3116	60	2525	53.1802	300
30 Leucine	-38.6	-9.3	3174	390	2595	54.3797	308
31 Isoleucine	-38.6	-9.8	3160	250	2565	54.2891	304
Second Acid Dissociation of Amino-Acids.							
32 Glycine	-28.5	-9.2	13328	10600	4175	38.8710	671
33 Alanine (i)	-11.1	-5.6	13455	11800	3078	14.3118	1271
33 Alanine (ii)	-20.0	-6.4	13449	11540	3826	30.1866	873
34 α-NH ₂ -n-Butyric	-16.3	-9.0	13400	10750	3400	21.8654	956
35 α-NH ₂ -n-Valeric	-6.6	-8.4	13370	10870	2800	7.7500	1940
36 Norleucine	-16.3	-8.3	13406	10940	3448	21.0224	970
37 α-NH ₂ -iso-butyric	-16.3	-7.8	13911	11580	3587	22.1177	1010
38 Valine	-16.3	-8.7	13249	10670	3389	20.9395	953
39 Leucine	-16.3	-8.1	13283	10880	3433	21.0621	965
40 Isoleucine	-16.3	-8.4	13302	10790	3414	20.9843	960
Inorganic Acids.							
41 Phosphoric (1st stage)	-47.4	-15.7	2895	-1790	2691.8	65.7957	260.3
42 Phosphoric (2nd stage)	-47.0	-30.2	9823	820	3236.4	62.0459	315.6
43 Metaboric	-49.7	-30.9	12591	3370	3967.3	65.9317	365.9
Positively Charged Acids.							
44 Ammonium ion	0.0	-0.54	12562	12400	2706.0	-0.139	—
45 Monomethyl-ammonium ion	+ 7.5	-4.7	14484	13092	2374.0	-11.9634	—
46 Dimethyl-ammonium ion	+19.9	-9.5	14721	11880	1298.0	-31.1634	—
47 Trimethyl-ammonium ion	+41.0	-15.3	13384	8828	-740.5	-63.2534	—
48 Anilinium ion	0.0	+ 2.8	6265	7105	1553.0	0.614	—
49 o-Cl-anilinium ion	0.0	+ 8.1	3591	6007	1313.0	1.772	—

data and in some cases, notably for butyric acid, revised the final values of K . Assuming constancy of ΔC_p over the whole temperature range, we estimate the error in its evaluation for the fatty acids to be ± 0.5 cal./degree.

The data of Schaller were obtained by a conductivity method, and refer to classical "Ostwald" constants. We have taken the mean of his results at several dilutions. The work is not as reliable as more recent investigations, but it covers a wider temperature range. Furthermore, although the absolute values may be in considerable error, it seems likely that the deviations will be about the same at each temperature, so that it is justifiable to use the data for analysis of the temperature dependence. The uncertainty in ΔC_p is about ± 2 cal. per degree.

The values for the amino acids were obtained by Harned's method, but are much less reliable than Harned's own measurements, and consequently in most cases the values of ΔC_p can only be determined to ± 5 cal./degree.

The values of ΔH and ΔC_p which we have tabulated are determined by the first and second differential coefficients of the free energy changes, it is therefore important that in two instances we have confirmation of these values from direct thermal measurements. For the ionisation of water Pitzer,⁵ from a review of measurements of specific heats and of heats of neutralisation,^{8,9} has concluded that $\Delta H_{298.1} = 13,358$, while $\Delta C_p = -50$, compared with 13,490 and -51 given in Table I.

For acetic acid Richards and Mair,¹⁰ using an incorrect method of extrapolation to zero concentration, found $\Delta H_{298.1} = 13,650$; a correct

* Throughout, heat and energy changes are expressed in cal./gram-molecule; heat capacity and entropy changes in cal./gram molecule degree.

† We have taken $R = 1.986$ cal./deg., $T = t^\circ \text{C.} + 273.1$ for these calculations.

⁷ (1) Harned and Hamer, *J. Am. Chem. Soc.*, 1933, **55**, 2194; Harned and Copson, *ibid.*, 1933, **55**, 4496; Harned and Mannweiler, *ibid.*, 1935, **57**, 1873; Harned and Donelson, *ibid.*, 1937, **59**, 1280; Harned and Geary, *ibid.*, 1937, **59**, 2032; Harned and Cook, *ibid.*, 1937, **59**, 2304.

(2) Harned and Embree, *ibid.*, 1934, **56**, 1042.

(3) Harned and Ehlers, *ibid.*, 1932, **54**, 1350; Harned and Ehlers, *ibid.*, 1933, **55**, 652.

(4) Harned and Ehlers, *ibid.*, 1933, **55**, 2379.

(5) Harned and Sutherland, *ibid.*, 1934, **56**, 2039.

(6) Wright, *ibid.*, 1934, **56**, 314.

(7) Martin and Tartar, *ibid.*, 1937, **59**, 2672; Nims and Smith, *J. Biol. Chem.*, 1936, **113**, 145.

(8) Nims, *J. Am. Chem. Soc.*, 1936, **58**, 987.

(9)-(15), (17)-(22) Schaller, *Z. physik. Chem.*, 1898, **25**, 497.

(16) Euler, *ibid.*, 1898, **21**, 257.

(23), (32) Owen, *J. Am. Chem. Soc.*, 1934, **56**, 24.

(24), (33) (i) Nims and Smith, *J. Biol. Chem.*, 1933, **101**, 401.

(24) (33) (ii), (25)-(31), (34)-(40) Smith, Taylor and Smith, *ibid.*, 1937, **122**, 109.

(41) Nims, *J. Am. Chem. Soc.*, 1934, **56**, 1110.

(42) Nims, *ibid.*, 1933, **55**, 1946.

(43) Owen, *ibid.*, 1934, **56**, 1695.

(44) Everett and Wynne-Jones, *Proc. Roy. Soc., A*, 1938, **169**, 190.

(45)-(47) Everett and Wynne-Jones (*unpublished*).

(48) Pedersen, *K. danske vidensk. Selsk. Skr.*, 1937, **14**, 9.

(49) Pedersen, *ibid.*, 1937, **15**, 3.

⁸ Rossini, *Bur. Standards J. Research*, 1931, **6**, 847.

⁹ Rossini, *ibid.*, 1931, **7**, 47.

¹⁰ Richards and Mair, *J. Am. Chem. Soc.*, 1929, **51**, 737.

extrapolation yields the value 13,570. From specific heat data, which have been reviewed by Rossini,¹¹ the heat capacity change for the neutralisation is -15 , and consequently $\Delta H_{298.1} = 13,495$ which, combined with $\Delta H_{298.1} = 13,358$ for the ionisation of water, gives

$$\Delta H_{298.1} = -137$$

for the ionisation of acetic acid, and ΔC_p for the same reaction is -35 . These values have to be compared with the values $\Delta H_{298.1} = -100$ and $\Delta C_p = -36.6$ which are given in Table I.

It is evident that the agreement is satisfactory.

3. Other Methods of Representing the Experimental Data.

Harned and his collaborators represented their early results in the form

$$\log K = \frac{a}{T} + b \log T + cT + d \quad (11)$$

which is derived on the assumption that ΔH_T is given by

$$\begin{aligned}\Delta H_T &= a' + b'T + c'T^2, \\ \Delta C_p &= b' + 2c'T.\end{aligned}$$

and that

Equations of this type were shown to represent the data well over the temperature range examined, but as we have shown there is no need to assume a temperature dependence of ΔC_p in this range. Examination of Table II indicates that equation (3), which involves the assumption of a constant ΔC_p , gives at least as good a representation of the data as Harned's four constant equation.

Later, Harned and Embree⁶ showed that the curves of $\log K$ against T for most acids have approximately the same shape, and that they can be represented by a general parabolic equation of the form

$$\log K - \log K_m = p(t - \theta)^2 \quad (12)$$

where K_m is the maximum value of K , θ °C. is the temperature at which this maximum occurs, and p is a constant which Harned and Embree took as $-5 \times 10^{-5} \text{ deg.}^{-2}$ for all acids. Although this equation is found to represent the data fairly well over a short range of temperature near the maximum, it was advanced as a purely empirical equation. It is, however, related to equation (3), as may be seen in the following way.

At the temperature, T_m , at which K is a maximum, we have

$$\ln K_m = \frac{A}{T_m} + \frac{\Delta C_p}{R} \ln T_m + B.$$

Combination of this with (3) gives

$$\ln K - \ln K_m = A \left(\frac{1}{T} - \frac{1}{T_m} \right) - \frac{\Delta C_p}{R} \ln \frac{T_m}{T},$$

in which the right side may be expanded in a power series

$$\ln K - \ln K_m = A \left(\frac{T_m - T}{T T_m} \right) - \frac{\Delta C_p}{R} \left\{ \frac{T_m - T}{T} - \frac{1}{2} \left(\frac{T_m - T}{T} \right)^2 + \dots \right\}.$$

For temperatures near the maximum we may neglect powers of $(T_m - T)/T$

¹¹ Rossini, *Bur. Standards J. Research*, 1930, 4, 313.

greater than the second, and, since $A = -\Delta H_0/R = \Delta C_p T_m/R$, the last equation becomes

$$\log K - \log K_m = \frac{1}{2} \cdot \frac{\Delta C_p}{2.303 RT^2} (T - T_m)^2 \quad (12)$$

which is of the same form as the Harned-Embreë equation with

$$p = \frac{1}{2} \cdot \frac{\Delta C_p}{2.303 RT^2} \quad (13)$$

On substituting the value of -40 cal./degree for ΔC_p and $300^\circ K$ for T , this gives $p = -4.9 \times 10^{-5}$ deg.⁻². Thus, equation (4) becomes essentially identical with Pitzer's form of (3) when

$$T \sim T_m \sim 300^\circ K.$$

TABLE II.
($\log K_{\text{obs.}} - \log K_{\text{calc.}} \times 10^4$.)

<i>t.</i>	0.	5.	10.	15.	20.	25.	30.	35.	40.	45.	50.	55.	60.	Σ v .
Formic														
Eqn. (3)	- 5	+ 5	+ 4	- 7	- 4	+ 6	-13	+ 3	-12	- 8	+ 4	+ 2	- 4	77
Eqn. (11)	-11	+17	+10	- 2	0	+ 5	+10	- 2	-20	-16	0	+ 13	+ 8	114
Acetic														
Eqn. (3)	- 5	+ 3	+ 3	- 4	- 6	- 2	+12	+ 1	+ 2	0	0	- 2	- 4	44
Eqn. (11)	-26	- 5	+ 3	0	+ 3	+ 7	+22	+10	+ 8	+ 4	0	- 9	- 14	111
Eqn. (4)	- 8	+ 8	+ 1	- 9	-14	-13	+ 2	- 4	+ 7	+23	+49	+80	+124	342
Eqn. (3), Pitzer's form)	+19	+20	+ 5	-14	-15	- 3	- 1	- 6	- 2	+ 1	+ 5	+ 13	+ 7	111
Propionic														
Eqn. (3)	- 9	+ 5	+13	+11	+ 5	+ 9	+10	+ 9	- 8	-14	- 9	- 12	- 8	122
Eqn. (11)	- 3	+ 6	+ 9	+ 3	- 4	0	- 4	- 3	-17	-14	- 4	+ 4	+ 20	89
Butyric														
Eqn. (3)	- 5	+ 4	+ 2	+13	+ 1	+ 4	+ 4	- 7	-12	- 4	- 4	+ 2	- 7	69
Eqn. (4)	0	+ 3	+14	+ 8	-20	-23	-14	-28	-15	+ 6	+56	+108	+170	465
Eqn. (3), Pitzer's form)	+19	+15	- 7	0	-26	-26	-26	-34	-32	-12	- 5	+ 13	+ 25	238

<i>t.</i>	25.	40.	50.	60.	70.	80.	90.	99.	Σ v .
Benzoic, Eqn. (3)	-13	+47	-9	-23	-16	+24	+ 8	-15	155
<i>o</i> -Nitro-Benzoic Eqn. (3)	-52	+37	-54	-22	+16	+59	+39	-21	300
<i>m</i> -Toluic, Eqn. (3)	-19	-34	+17	- 3	- 4	+33	+23	-17	150

It would, of course, be possible to remove the restriction that the maximum occurs near $25^\circ C$. by adjusting the value of p . Owen ⁷⁽⁴³⁾ has suggested such a modification of the equation of Harned and Embree to get better representation of the data.

In another respect the equation of Harned and Embree is unsatisfactory. Equation (12) shows that if we regard p as a constant independent of temperature, then ΔC_p is proportional to T^2 —a relation which predicts a very large temperature dependence of ΔC_p , quite incompatible

with the data. A similar conclusion has been reached by Walde,¹² who showed that the values of p required to represent the data accurately must vary considerably with the temperature.

It is of interest to compare the various equations which have been proposed to represent the temperature dependence of dissociation constants. This is done in Table II in which we give the differences between the observed and calculated values of $\log K$ for several acids, using the different equations mentioned above. The last column contains the sum of the absolute values of the differences.

In Fig. 3 the data for butyric acid are shown graphically. This acid has been chosen since for it the relative accuracies of the various equations are most clearly shown; it is seen that equation (3) of this paper

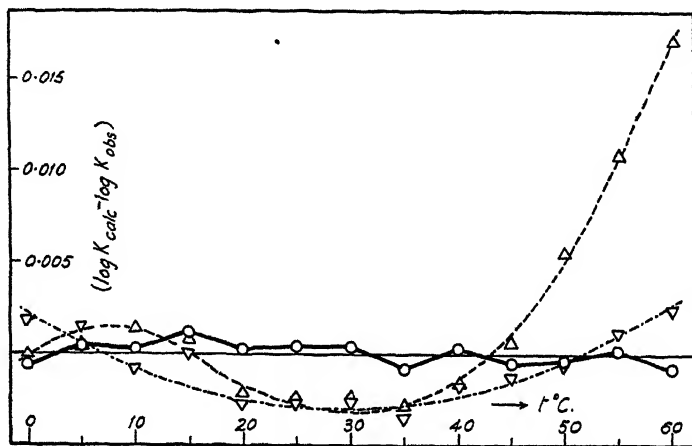


FIG. 3.
($\log K_{\text{calc.}} - \log K_{\text{obs.}}$) v. $t^{\circ}\text{C.}$
Butyric Acid.

- Eqn. 3.
△ Eqn. 4 (Harned and Embree).
▽ Pitzer's form of (3).

gives the best representation of the data when the appropriate values of A , B and ΔC_p are substituted. This equation is also best for the other fatty acids, although the superiority is not so marked as in the case of butyric acid.

4. The Significance of ΔC_p .

As we have previously pointed out, Born's equation,¹³ based on simple electrostatic principles, is incapable of accounting for the large negative values of ΔC_p . This we have therefore attributed to the orientation of the solvent molecules round the ions; interaction with the solvent is considered to result in the contributions to the specific heat from the rotations of these molecules being lost, thus causing a further decrease in the heat capacity of the system.

¹² Walde, *J. phys. Chem.*, 1935, 39, 477.

¹³ Born, *Z. Physik*, 1920, 1, 45.

The expression for the change in heat capacity derived from Born's equation is

$$(\Delta C_p)_{B.C.} = \frac{z^2 \epsilon^2}{2r} \cdot T \frac{\partial^2}{\partial T^2} \left(\frac{1}{D} \right) \quad (14)$$

and to evaluate this we require to know how the dielectric constant of the solvent varies with temperature. It is of interest to see that both the form of the right side of (14) and the values of ΔC_p calculated from it are very sensitive to the relation we assume between D and T .

The equation most commonly employed is that suggested by Abegg¹⁴

$$\log D = A - bT \quad (15)$$

which on substitution in (10) yields

$$(\Delta C_p)_{B.C.} = -\frac{z^2 \epsilon^2}{2r} \cdot (2.303 b)^2 \cdot \frac{T}{D} \quad (16)$$

Taking $b = 0.0020 \text{ deg.}^{-1}$ and $r = 1 \text{ \AA.}$, this equation predicts a value for $(\Delta C_p)_{B.C.}$ of -26 cal./degree for a dissociation reaction in water at 25° C. We see, however, that a large temperature dependence is indicated.

An alternative form of equation which we find represents very closely the data of Kockel¹⁵ and of Lattey, Gatty and Davis,¹⁶ but not so closely the recent data of Wyman and Ingalls,¹⁷ is

$$\log D = A - B \log T \quad (17)$$

which gives ΔC_p in the form

$$(\Delta C_p)_{B.C.} = -\frac{z^2 \epsilon^2}{2r} \cdot \frac{B(B-1)}{DT} \quad (18)$$

Putting $B = 1.475$ and $r = 1 \text{ \AA.}$, the calculated value of $(\Delta C_p)_{B.C.}$ is -10 cal./degree in water at 25° C. Furthermore, since DT varies only slowly with temperature, this equation predicts an almost temperature independent (ΔC_p) in agreement with the conclusions arrived at earlier in this paper.

Of course, if Born's charging term is small, corresponding to an ionic radius of 4 or 5 \AA. , we cannot use the temperature independence of ΔC_p as an argument in support of equation (17) as against (15).

Since simple electrostatic considerations based on Born's equation cannot give us values large enough to account for the whole of the heat capacity change we examine next orientation effects which seem capable of accounting for the remaining portion of ΔC_p .

In general terms we see that a change in structure of a solvent may give rise to a large change in heat capacity—the heat capacity change on freezing water is -9 cal./degree per mole. It is possible to regard the molecules oriented by an ion as resembling those in ice, differing from ice molecules mainly in that they may still retain their translational degrees of freedom. Part of the 9 cal. difference between ice and water is presumably due to effective loss of translational degrees of freedom, and if we put this contribution at $3/2R$, the decrease due to the effective loss of rotational degrees of freedom is about 6 cal./degree per mole. Taking this as equal to the loss in heat capacity due to the

¹⁴ Abegg, *Wied. Ann.*, 1897, 60, 54.

¹⁵ Kockel, *Ann. Physik*, 1925, 87, 417.

¹⁶ Lattey, Gatty and Davies, *Phil. Mag.*, 1931, 12, 1019.

¹⁷ Wyman and Ingalls, *J. Am. Chem. Soc.*, 1938, 60, 1182.

orientation of water molecules round an ion, we see that if each ion has a co-ordination number of four, the heat capacity change for the ionisation of an uncharged acid will be about -48 cal./degree; this is roughly equal to the observed changes.

For the purposes of our discussion we propose to retain the formal division of ΔC_p into two portions, the change calculated from Born's equation, and that due to the orientation of the solvent molecules round the ions. While we find this a convenient basis for discussion, we realise that this separation of ΔC_p into simple electrostatic and orientational contributions is arbitrary, since all dielectric phenomena are concerned with the restriction of movement of the molecules of the medium. The division consists essentially in considering the value of ΔC_p calculated on the assumption that the solvent retains its macroscopic dielectric constant right up to the hydration shell of the ion, and then regarding the difference between this and the observed change as due to more or less complete orientation of the solvent molecules in the neighbourhood of the ions (*i.e.*, to saturation of the dielectric).

We obtain further support for the above interpretation of ΔC_p from a consideration of the effect on ΔC_p of change of solvent. In Table III

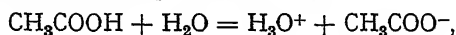
TABLE III.—DISSOCIATION OF ACETIC ACID IN DIOXANE WATER AND METHYL ALCOHOL WATER MIXTURES.

THERMODYNAMIC FUNCTIONS.

Solvent.	$+\Delta C_p$ (cal./deg.).	$+\Delta S_{298-1}^0$ (cal./deg.).	ΔC_{298-1}^0 (cal.).	ΔH_{298-1} (cal.).	$-A.$	$B.$
Water	-36.6	-22.1	6483	-100	2359	47.6856
20 % Dioxane .	-39.8	-24.4	7211	-70	2579	52.8474
45 % Dioxane .	-43.0	-29.8	8598	-300	2724	56.2759
70 % Dioxane .	-46.6	-39.9	11290	-600	2909	59.3522
10 % MeOH . .	-45.4	-22.4	6685	0	2956	60.4267
20 % MeOH . .	-48.2	-22.6	6924	160	3169	65.4282

are given the results of the analysis of the data of Harned and Embree,¹⁸ and of Harned and Kazajian¹⁹ for the dissociation of acetic acid in methyl alcohol water and dioxane water mixtures respectively. At present these are the only data available on temperature coefficients in solvents other than water.

The ionisation of acetic acid in dioxane water mixtures is essentially the same process as that in pure water, *viz.* :



and we may regard the hydration shell as remaining unchanged. The variation of ΔC_p with the solvent will then be caused by the change in dielectric constant, and may be calculated from Born's equation. We have expressed the results of Åkerlöf and Short²⁰ for the dielectric constant of dioxane-water mixtures in the form of equation (17); the equations are given in the table below. From these relations we have deduced values of the contributions to ΔC_p of Born's charging process setting $r = 5$ Å. which is arbitrarily taken for the radius of the hydrated

¹⁸ Harned and Embree, *J. Am. Chem. Soc.*, 1935, **57**, 1669.

¹⁹ Harned and Kazajian, *ibid.*, 1936, **58**, 1912.

²⁰ Åkerlöf and Short, *ibid.*, 1941.

ion; these calculated values are given in column 3. Column 4 of Table IV contains observed values of ΔC_p , less the figures in column 3;

TABLE IV.

Solvent.	Equation for D .	$(\Delta C_p)_{B.O.}$ (cal./deg.).	$(\Delta C_p)_{obs.} - (\Delta C_p)_{B.O.}$ (cal./deg.).
Water . . .	$\log D = 5.539 - 1.475 \log T$	- 2	-34.6
20 % Dioxane .	$\log D = 5.864 - 1.65 \log T$	- 4	-36.0
45 % Dioxane .	$\log D = 5.872 - 1.74 \log T$	- 8	-35.0
70 % Dioxane .	$\log D = 5.874 - 1.87 \log T$	-20	-27.0

these should represent the contributions to ΔC_p from the orientation of the water molecules.

The essential agreement of the first three figures in the last column shows that it is reasonable to interpret the change of ΔC_p on an electrostatic basis, and also indicates that the simple electrostatic term is not large, particularly in water.

The data for methyl alcohol water mixtures do not extend over a sufficient range of dielectric constant to be usefully discussed at present; they do, however, appear to exhibit the same type of behaviour as the dioxane-water mixtures, although we may expect complications, since there is the possibility of both alcohol and water molecules being oriented.

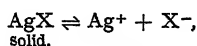
5. Value of ΔC_p Related to the Structure of an Acid.

Without a complete theory of the heat capacities of dissolved substances it is impossible to give a quantitative explanation of the variations in heat capacity changes corresponding to the various ionic dissociations. It is indeed noteworthy that to a fair approximation the value of ΔC_p is -40 cal./degree for all the carboxylic acids considered in this paper. This undoubtedly arises from the fact that the ionisation process results in the disappearance of a neutral molecule and the formation in all cases of a hydrogen ion and of an anion closely similar to the neutral molecule in all respects except that it carries a charge.*

Nevertheless, it is interesting to consider the differences shown in Table I, and it is possible to account for them in a qualitative way. As we have seen, the contribution to the heat capacity change from Born's charging process is small, so that for acids of approximately the same size, variations in the individual values of ΔC_p must be due to the differences between the orienting power of the respective anions, since that of the hydroxonium ion is the same for all acids.

The orientation of solvent molecules by an anion will be controlled by the electrostatic potential near the surface of the ion, which, in turn, will be largely dependent on the following two factors:

* Further evidence that the change in heat capacity is essentially due to the formation of two ions with the disappearance of a neutral molecule is afforded by recent data for the reaction



for which Owen and Brinkley (*J. Am. Chem. Soc.*, 1938, **60**, 2233) obtain values of ΔC_p of between -35 and -40 cal./degree at 25° for the various halides.

(a) the distribution of charge in the ion—the more localised the charge, the stronger the orienting power;

(b) a steric factor which may arise as a result of groups in the ion screening the solvent molecules from the effect of the localised negative charge. If a group has such a screening effect the heat capacity change for the ionisation will be diminished.

As a consequence of the variations in the electrostatic potential in the anions of related acids, we may expect to find a correspondence between the changes in ΔC_p and in acid strength of which we regard ΔH_0 as a rough measure. An increase in the electrostatic potential will cause more powerful orientation of solvent molecules, and hence a larger negative value of ΔC_p , but it will also make the removal of a proton

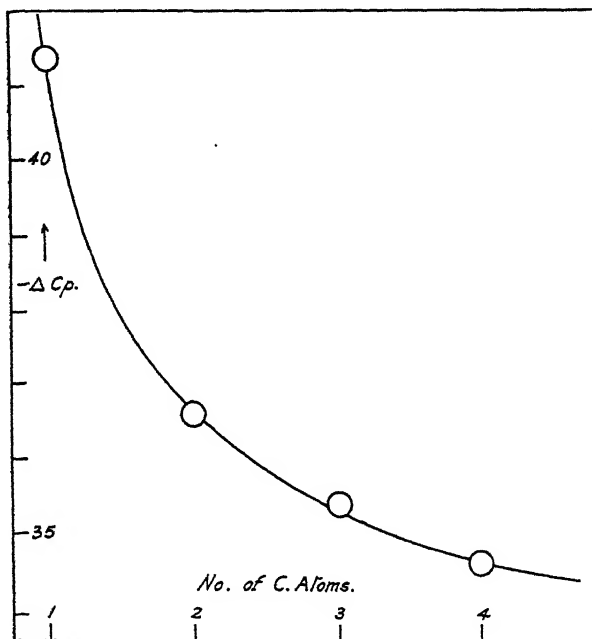


FIG. 4.
 ΔC_p for Fatty Acids v. No. of C atoms.

more difficult and therefore increase ΔH_0 . Equation (10) shows that the ratio of ΔH_0 to ΔC_p determines the temperature of the maximum value of K , so we shall expect this temperature, T_m , to be largely independent of the strength of the acid. This is found to be true—of the 21 carboxylic acids we have examined, 16 have values of T_m lying between 270° K. and 310° K. The exceptions are the *o*-substituted benzoic acids in which we might expect to find disturbing steric effects.

The variation of ΔC_p in certain series presents several interesting features. For the fatty acids, as shown in Fig. 4, ΔC_p varies from -41.4 cal./deg. for formic acid to an approximately constant value of -34 cal./deg. for the higher members of the series, and this seems to be a consequence of the steric factor. The introduction of a methyl group into the formate ion will result in a partial screening of the water

molecules from the field of the charge, while further lengthening of the hydrocarbon chain produces a smaller additional effect.

In the toluic acids the values of $-\Delta C_p$ increase regularly from the *o*- to the *p*-acid; as the screening effect of the methyl group will decrease in the same order we should expect just such a change in ΔC_p .

For the ionisation of lactic, glycolic and salicylic acids ΔC_p is numerically much larger than for the corresponding unsubstituted acids. The presence of the hydroxyl group thus appears to favour the orientation of water molecules, probably on account of the capability of the hydroxyl group forming a hydrogen bond with the oxygen of a water molecule.

With the benzoic acids the presence of substituents in the ring may give rise to inductive and tautomeric effects which will tend to increase or decrease the potential at the carboxyl group according to the nature of the substituent groups and their position in the ring. Superimposed on this effect will be the steric factor which will in all cases tend to reduce the value of $-\Delta C_p$, being most effective in the *ortho*-position. Examination of Table V shows that, for the limited data available, the effects are those which would be expected on the basis of modern electronic theories.

TABLE V.

	<i>o</i> -.			<i>m</i> -.			<i>p</i> -.		
	ΔC_p (cal./deg.).	ΔH_0 (cal.).	$\Delta G_{298.1}^0$ (cal.).	ΔC_p (cal./deg.).	ΔH_0 (cal.).	$\Delta G_{298.1}^0$ (cal.).	ΔC_p (cal./deg.).	ΔH_0 (cal.).	$\Delta G_{298.1}^0$ (cal.).
Cl	-28	5970	3926	—	—	—	—	—	—
I	-22	3770	3903	-37	11220	5260	—	—	—
NO ₂	-24	3710	2980	-37	11400	4703	—	—	—
OH	-48	15250	4055	-30	9076	5561	—	—	—
OCH ₃	—	—	—	—	—	—	-50	15600	6110

Benzoic; $\Delta C_p = -36$ cal./deg., $\Delta H_0 = 10800$ cal., $\Delta G_{298.1}^0 = 5682$ cal.

If we assume that the toluic acids are influenced only by the steric factor, then we can assign to the effect on $-\Delta C_p$ the approximate values of -5 , -3 and 0 cal./deg. for groups substituted in the *ortho*-, *meta*- and *para*-positions respectively. The electrostatic effects would then be about -5 and $+4$ cal./deg. for halogen or nitro substitution in the *ortho*- and *meta*-positions respectively. For substitution of hydroxyl this factor causes an increase in $-\Delta C_p$ of 17 cal./deg. in the *ortho*-position, and a decrease of 3 cal./deg. in the *meta*-position, while *para*-substituted methoxyl has an electrostatic factor of 14 cal./deg.

6. Strengths of Organic Acids and their Structure.

It has been the common practice to regard the dissociation constant of an acid in water at 25° C. as a measure of its intrinsic strength and on this basis theories have been developed correlating acid strength and chemical constitution. The simple electronic conceptions of the inductive and mesomeric effects were found to be inadequate; the anomalies require for their explanation the postulation of rather special effects for whose existence there is often very little corroborative evidence. This

is somewhat unsatisfactory, and emphasises the need for a closer examination of the fundamental assumption which is involved.

This assumption may be criticised mainly on two accounts. Firstly, the dissociation constant of one acid relative to another in the same solvent and at the same temperature is found to depend upon the solvent employed. This effect has been discussed by Wynne-Jones.²¹ He showed that for two acids, HA_1 and HA_2 , on plotting $\log (K_{A1}/K_{A2})$ against the reciprocal of the dielectric constant of the solvent, a straight line is obtained. On extrapolation to $1/D = 0$ this gives a value of $\log (K_{A1}/K_{A2})$, which it was suggested should be regarded as the true value of the strength of one acid relative to another at the given temperature.

Secondly, the relative strengths of two acids may not be independent of temperature. Attention was first drawn to this possibility by Hammett,²² who reviewed the data for a number of acids, and pointed out that a theory based on heats of reaction at 25° C. would differ widely from one based on standard free energy changes. The use of dissociation constant data in discussing the structure of acids would only be possible if the effect of a substituent on the heat of ionisation were the same as its effect on the free energy change. This has also been discussed by Baker and Dippy;²³ Baker criticises the use of data at 25° C., and an answer is made by Dippy.

As an argument in support of his view Dippy says that in point of fact there is no experimental evidence that relative strengths do depend on the temperature of comparison. This statement is invalidated by a closer examination of the data. To illustrate this we have plotted in Fig. 5 the values of $\log K$ for acetic and butyric acids against temperature; the shapes of the curves below 0° C. have been calculated from our empirical equations. The third curve is that of the relative strengths of the two acids; there is no question that this curve must cut the axis at about -10° C., and that below this temperature butyric acid is stronger than acetic.

It is now apparent that no justification exists, either on theoretical or experimental grounds for the choice of an arbitrary temperature at which to compare acid strengths.

Furthermore, the use of the maximum values of $\log K$, as suggested by Harned and Embree,⁵ has no theoretical basis.

The values of ΔH_0 obtained for the various acids as a result of our analysis may now be discussed in relation to the strengths of acids. If it were possible to assume that ΔC_p remained constant for all temperatures down to absolute zero, then ΔH_0 would be equal to ΔG_0^0 , the standard free energy of ionisation at absolute zero. We should then have Hammett's condition satisfied that the effect of a substituent on heat and free energy changes must be the same in order to use the data for discussion of intrinsic acid strengths. Unfortunately, this is an unjustifiable assumption, so that in the first place we cannot expect to be able to attach any theoretical importance to the *absolute* values of ΔH_0 .

At low temperatures, however, we might expect the heat capacities of the anions to vary in a rather similar manner in any given solvent.

²¹ Wynne-Jones, *Proc. Roy. Soc.*, 1933, 140, 440.

²² Hammett, *J. Chem. Physics*, 1936, 4, 613.

²³ Baker, Dippy and Page, *J. Chem. Soc.*, 1937, 1774; cf. ref. 25.

It seems probable, therefore, that the calculated values of ΔH_0 will fall in the same order as the true values of ΔH_0 or ΔG_0^0 . The possibility thus arises of employing the values of ΔH_0 calculated above as measures of the relative intrinsic strengths of acids.

The effect of a substituent on the heat and free-energy change of ionisation will also be the same when ΔG^0 has a maximum value (*i.e.* $\Delta S^0 = 0$). Since our analysis shows that in most cases the values of ΔG_{\max}^0 and of ΔH_0 are in the same relative order, we shall confine our discussion to the values of ΔH_0 .

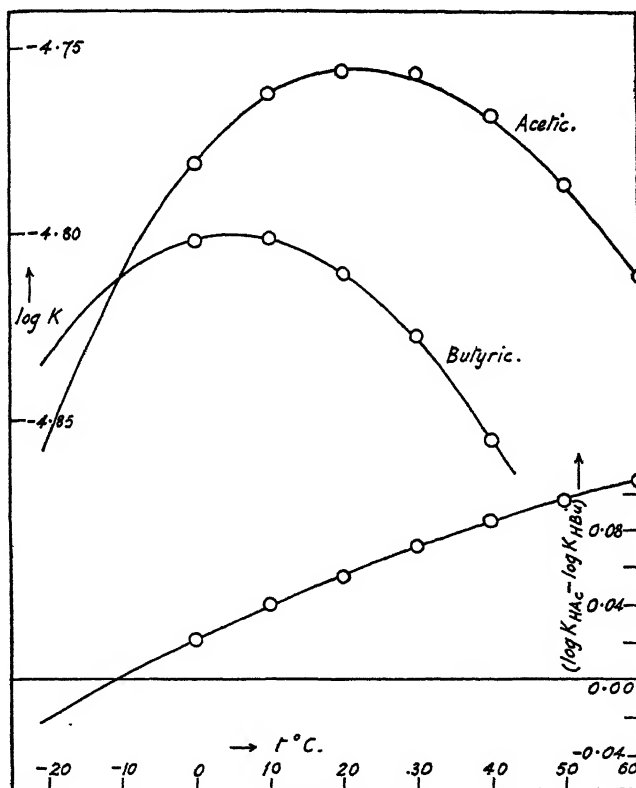


FIG. 5.

Top curve :	$\log K_{\text{acetic}}$	$v. \ t^{\circ} \text{C.}$
Middle curve	$\log K_{\text{butyric}}$	$v. \ t^{\circ} \text{C.}$
Lower curve :	$\log K_{\text{HAc}} - \log K_{\text{HBu}}$	$v. \ t^{\circ} \text{C.}$

In the following paragraphs we have examined the possibilities of this basis of comparison. We must emphasise, however, that our suggestions are tentative and provisional until further accurate data on the variation of dissociation constants over a wide range of temperature become available. In general it can be said, as far as the available data allow comparison, that the strengths of acids as measured by ΔH_0 exhibit much more regularity than those deduced from measurements at 25°C. Many of the apparent anomalies which have necessitated modifications of the theory based on values of $\log K_{25}$ disappear in the extrapolation.

Fatty Acids.

At 25° C. the order of the strengths of the fatty acids is

formic > acetic > butyric > propionic.

The apparently anomalous position of butyric acid has been discussed by Bennett and Mosses,²⁴ and by Dippy.²⁵ The explanations advanced are, however, by no means convincing.

As we have shown, the relative strengths of butyric and acetic acids change with temperature. This is also true of the other fatty acids, although the curves cut at much lower temperatures (100° K. to 200° K.); but uncertainties in the behaviour of ΔC_p will probably not yet be serious.

The values of ΔH_0 indicate intrinsic strengths in the order

butyric > propionic > acetic > formic.

The order is now regular, and it is worth noting that the only one of the thermodynamic functions showing any anomaly in this series is the free energy change at room temperature; the values of ΔC_p , ΔS_{298-1}^0 and ΔH_{298-1} all form a regular series.

Chloracetic Acid.

The increase of the strength of a fatty acid as a result of halogen substitution is regarded as due to the influence of the halogen-carbon dipole in decreasing the strength of binding of a proton to the carboxyl group. The data in Table I indicate that the effect is largely on the values of ΔC_p and ΔS^0 , and that although the ΔH_0 values do confirm the enhanced strength of chloracetic acid, the magnitude of the effect is probably less than the values of ΔG_{298-1}^0 would suggest.

We have already mentioned that we do not place too much emphasis on the values of ΔH_0 ; especially for acetic and chloracetic acids it is quite possible that at low temperatures the form of the $\Delta C_p - T$ curves will differ appreciably; such deviations will be less likely for the simple fatty acids.

Toluic Acids.

The order of strengths at 25° C. is

o-toluic > benzoic > *m*-toluic > *p*-toluic.

The position of *o*-toluic acid has been discussed from a same standpoint as that of butyric acid.²⁶

If we take ΔH_0 as our basis of comparison, we obtain the order

o-toluic > *m*-toluic > *p*-toluic \sim benzoic.

As in the case of the fatty acids, the introduction of a methyl group seems to cause an increase in acid strength. Furthermore, the effect appears to fall off with distance and in the para-position the methyl group has practically no effect.

Substituted Benzoic Acids.

The variations in ΔG_{298-1}^0 between the *ortho*-substituted halogen and nitro-benzoic acids are large, and the values of ΔC_p such that the order

²⁴ Bennett and Mosses, *J. Chem. Soc.*, 1930, 2364.

²⁵ Dippy, *ibid.*, 1938, 1222.

²⁶ Dippy, Evans, Gordon, Lewis and Watson, *ibid.*, 1937, 1421.

of strengths remains unchanged on extrapolation to low temperatures. For the *meta*-substituted acids, however, while the values of $\Delta G_{298.1}^0$ indicate that the *meta*-nitro and *meta*-iodo acids are stronger than benzoic, the ΔH_0 values show a small decrease in strength. Similarly, we see that salicylic acid is weaker than benzoic, while *m*-hydroxybenzoic acid is slightly stronger.

This would seem consistent with the general observation that *meta*-substitution has an effect opposite to *ortho*- and *para*-substitution.

In accordance with expectations, anisic acid is considerably weaker than benzoic.

Further correlation of the strengths of these acids with their structure is probably not justified with the rather meagre data at our disposal.

7. The Significance of ΔS^0 .

The fact that the heat and entropy changes of an ionic reaction are not identical has been known for a long time, but it is only within recent years that any attention has been paid to these differences. Thermodynamically, the difference between the heat and the free energy is the entropy term $T\Delta S^0$, which is also related to the temperature coefficient of the free energy by the equation

$$\Delta S^0 = -d(\Delta G^0)/dT \quad . \quad . \quad . \quad (19)$$

Latimer and his co-workers have obtained values of the entropy of solution of many inorganic ions in water, and these values are all negative and also depend upon the ionic radius and charge in a way which has led Latimer²⁷ to suppose that the entropy can be interpreted purely in terms of Born's charging process. Eley and Evans,²⁸ on the other hand, have considered the orientation of solvent molecules around the ions, and have arrived at values for the entropy which are in fair agreement with experiment.*

A standpoint similar to Latimer's has been adopted by Gurney,²⁹ who has discussed specifically the temperature dependence of the dissociation constants of weak acids and has shown that, if the dissociation energy is split into an electrostatic and a non-electrostatic term, it is possible to give a qualitative explanation of the maximum in the dissociation constant-temperature curve of a weak electrolyte. His discussion is based on the assumption that, while the non-electrostatic energy required for dissociation is independent of temperature, the electrostatic energy increases with temperature. The standard free energy of dissociation is therefore given by the equation

$$\Delta G^0 = \Delta G_0^0 + G_{el} \quad . \quad . \quad . \quad (20)$$

where G_{el} is the electrostatic free energy, and should ideally be represented by Born's equation. In consequence of the assumed temperature independence of ΔG_0^0 we have

$$d(\Delta G^0)/dT = dG_{el}/dT \quad . \quad . \quad . \quad (21)$$

and Gurney regards this coefficient as a measure of the electrostatic energy.

²⁷ Latimer, Pitzer and Slansky, *J. Chem. Physics*, 1939, 7, 108.

²⁸ Eley and Evans, *Trans. Faraday Soc.*, 1938, 34, 1093.

* We have examined the possibility of applying to the calculation of ionic heat capacities, the methods of Eley and Evans for the calculation of heats and entropies of solution of gaseous ions.

²⁹ Gurney, *J. Chem. Physics*, 1938, 6, 499.

The position of the maximum in K depends upon the relative importance of the electrostatic and non-electrostatic contributions to the free energy, and Gurney introduces a quantity, x , which is defined by the equation

$$x = -\log K_T / (d(\Delta G^0)/dT)_T \quad (22)$$

Of this function Gurney states that, as x is a measure of the ratio of the dissociation energy to the electrostatic energy, it should be a "smooth function" of the temperature at which K is a maximum. That this is so

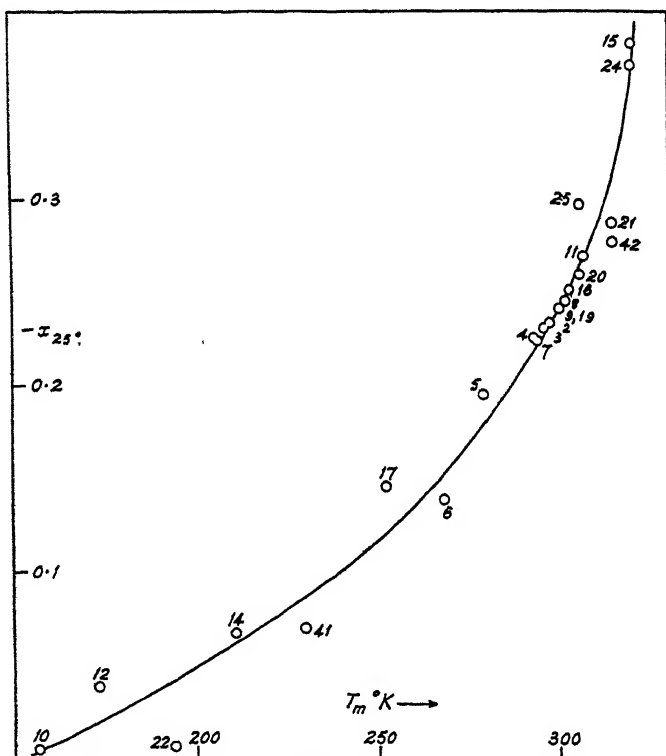


FIG. 6.
 $-x$ v. T_m .
 Numbers correspond to Table I.

is shown in Fig. 6, and Gurney regards this as proof of the correctness of his treatment.

To see the real significance of Gurney's assumptions, we must recall that the temperature coefficient of the free energy change is the entropy change of the process, and therefore the basic assumptions are that for non-ionic and isoelectric * processes, the values of ΔS^0 and ΔC_p are zero. The function, x , can also be expressed in simpler form by using thermodynamic relationships, which give us

$$x_T = -\frac{1}{2.303R} \cdot \left\{ \frac{1}{1 - (\Delta H/\Delta G^0)_T} \right\} \quad (23)$$

* Gurney describes as isoelectric those processes in which there is no change in the number of ions.

It can now be seen that, if the value of α is determined at the temperature corresponding to the maximum value of K , ΔH is necessarily zero, and hence α will be $-1/2 \cdot 303R$. If, therefore, we examine a number of acids with values of T_m not far removed from room temperature, and if for all these acids ΔC_p has the same sign, it is inevitable that α will be a "smooth function" of T_m ; such a relationship cannot, therefore, be regarded as justifying the splitting of the dissociation energy into electrostatic and non-electrostatic terms; still less does it prove the assumption that ΔS^0 is purely electrostatic.

There are three main arguments against this assumption of the electrostatic origin of ΔS^0 :—

- (1) Non-ionic and isoelectric equilibria often have quite large values of ΔS^0 .
- (2) The dependence of ΔS^0 upon the dielectric constant of the solvent suggests that only a part of the entropy is purely electrostatic.
- (3) For one ionic equilibrium we have found an extremely small value of ΔS^0 and, moreover, this changes sign within the experimental range.

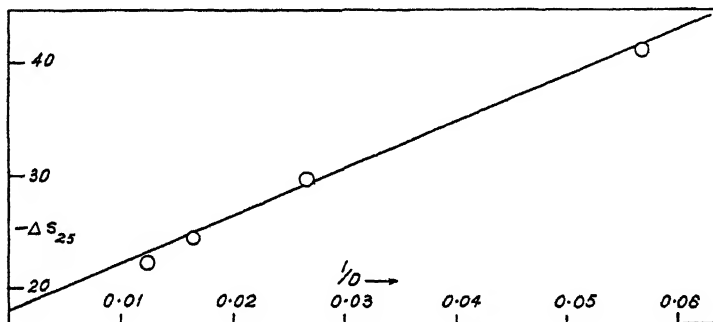
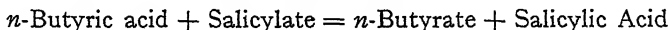
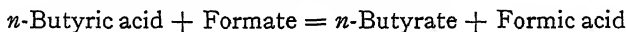


FIG. 7.
 $-\Delta S_{25^\circ}$ v. $(1/D)_{25^\circ}$.
 Acetic acid in dioxane water mixtures.

The evidence for the first statement is given on the one hand by such gaseous equilibria as the dissociation of hydrogen iodide and hydrogen selenide, and on the other hand by the values for isoelectric equilibria, which may be calculated from the data in Table I. For the dissociation of hydrogen iodide, Bodenstein's³⁰ results give $\Delta S^0 = 13.6$ cal./deg., while for hydrogen selenide³¹ $\Delta S^0 = 4$ cal./deg. For isoelectric equilibria we find that for the equilibrium,



$\Delta S^0 = -14.2$ cal./deg., and for the equilibrium,



$\Delta S^0 = -7.1$ cal./deg.

The dependence of ΔS^0 upon the dielectric constant can be determined from the results of Harned and Kazajian given in Table III. Their values of ΔS^0 are plotted against the reciprocal of the dielectric constant in Fig. 1, and it is seen that while there is a linear relationship,

³⁰ Bodenstein, *Z. physik. Chem.*, 1899, 29, 295.

³¹ Bodenstein, *ibid.*, 429.

there is not proportionality between these quantities and ΔS^0 is still large when $1/D = 0$.

The third argument is based upon the results of measurements which we have just completed of the dissociation constants of mono-, di-, and tri-methylamines. Details of this work, which has been carried out in the same way as our work on the basic strength of ammonia, will be published shortly; at present, we will simply mention that for the ionisation of trimethylamine we obtain $\Delta S^0 = -3.3$ cal./deg. at 25° C. and $\Delta C_p = -92$ cal./deg. It appears from our results that ΔS^0 actually changes sign at about 15° C.

It seems clear that the sign of ΔS^0 is not characteristic of ionic reactions, and that the attempted separation of an electrostatic energy of ionisation fails. This conclusion is not unexpected, as there is no method of deciding at what particular distance apart the separating atoms are to be regarded as electrically charged. The quantal distinction between exchange and coulomb forces is of no help to us, since this distinction is a mathematical device which is useful in a particular treatment, but has no physical basis.

In spite of the failure of Gurney's attempt to make a clear-cut separation of electrostatic and non-electrostatic forces, there are obvious differences between ionic and non-ionic equilibria, and from the data collected in this paper we can assert that for ionisation processes at room temperature the heat capacity is always negative and large and the entropy change is also usually negative. These two thermodynamic characteristics of ionisation processes are of considerable importance, and we shall expect them to be exhibited not only in equilibria, but also in reaction rates; in fact, there is already considerable evidence³² that in the rates of such reactions as the formation of quaternary ammonium salts the entropy changes are appreciable, and for other reactions heat capacity changes have been recorded.

We conclude that in any reaction there will usually be finite values of ΔS^0 and ΔC_p , but in ionisation processes occurring in a polar solvent the ionic charges produced will give rise to large negative values of these functions, primarily because of the powerful orientation of solvent molecules in the immediate neighbourhood of the ions. The resultant values of ΔS^0 and ΔC_p will therefore normally be negative and often large. The exact calculation of these quantities can be performed only by the methods of statistical mechanics, and at the moment presents considerable difficulties.

(*Added in proof.*) Harned and Owen³³ have just published a review of the thermo-dynamic properties of acid-base equilibria. Their values of the functions ΔG^0 , ΔS^0 , and ΔH are mostly in good agreement with ours, but their values of ΔC_p are widely different. This discrepancy is the result of their calculating ΔC_p not directly from the data but through their empirical equation (4). In our discussion we have shown that this equation is only an approximation and that it must lead to erroneous values of ΔC_p .

Summary.

The experimental data for the electrolytic dissociation of weak acids have been subjected to a careful analysis from which we have obtained values of ΔG^0 , ΔH , ΔS^0 , and ΔC_p for the various equilibria.

³² Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, 3, 492.

³³ Harned and Owen, *Chem. Rev.*, 1939, 25, 31.

It is noteworthy that for the ionisation of uncharged acids, such as acetic acid, the values at room temperature of ΔS^0 and ΔC_p are usually negative.

The sign and magnitude of the heat capacity change is to be explained by the orientation of solvent molecules around the ions. We have also considered in general terms the relationship between the molecular structure and the various thermodynamic quantities and have shown that, for a proper comparison of the strengths of acids, it is necessary to take into account not merely the dissociation constants at a particular temperature but the values of all the thermodynamic functions.

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THE GROWTH OF CRYSTALS FROM A STREAM OF VAPOUR.

BY R. N. HAWARD.

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The mechanism of the growth of crystals from the vapour is a problem which has become of interest since Volmer¹ showed that with mercury the molecules on the surface could be mobile, and since Kossel² and Stranski³ elaborated their theory of crystal growth. The experiments of Alty⁴ have shown that in certain cases the rate of evaporation of a crystal mass can be much less than the rate at which molecules strike its surface when it is surrounded by its vapours in equilibrium, consequently there must be a certain difficulty in the transition of a molecule from the crystal lattice to the vapour and vice versa. The present series of quantitative experiments has been made using a rough molecular stream to give thick layers of crystalline deposits on a cooled target in order to obtain in a direct way information concerning the details of the mechanism of steady crystal growth.

Experimental Method.

The essential part of the apparatus is shown in Fig. 1; the whole of it was contained in an outer vessel which was surrounded by liquid air and which could be evacuated. It consisted of a furnace with a small orifice in its lid and a cooled target 2.5 cm. wide situated above the furnace at a distance 2.50 cm. from the orifice. The furnace could be removed and weighed; when it was heated in a vacuum the vapour of the substance in it was emitted from the orifice and a certain fraction of the stream struck the target. In order to use the arrangement to investigate the condensation on the target this fraction had to be known.

As a step towards investigating the nature of this stream, experiments were made with a hollow target fitted with a perforated lid. The ratio of the area of the holes in this lid to the area of its surface was 0.190. If every molecule striking the surface of the target condensed then the

¹ Volmer and Esterman, *Z. Physik*, 1921, 7, 13.

² Kossel, *Nachr. Göttingen Ges.*, 1927.

³ Stranski, *Z. physik. Chem.*, 1928, 136. Stranski and Kaischew, *Physik. Z.*, 1935, 36, 393.

⁴ Alty, *P.R.S.*, 1937, 161, 68.

ratio of the deposits inside and outside the target should be 0.190, and this occurred with salicylic acid at temperatures below -40°C .; at these temperatures also the deposit inside the target had the form of sharply defined patches opposite the holes in the lid. At higher temperatures the whole behaviour became irregular and the deposits inside the target diffuse. In the following work it is assumed that all molecules

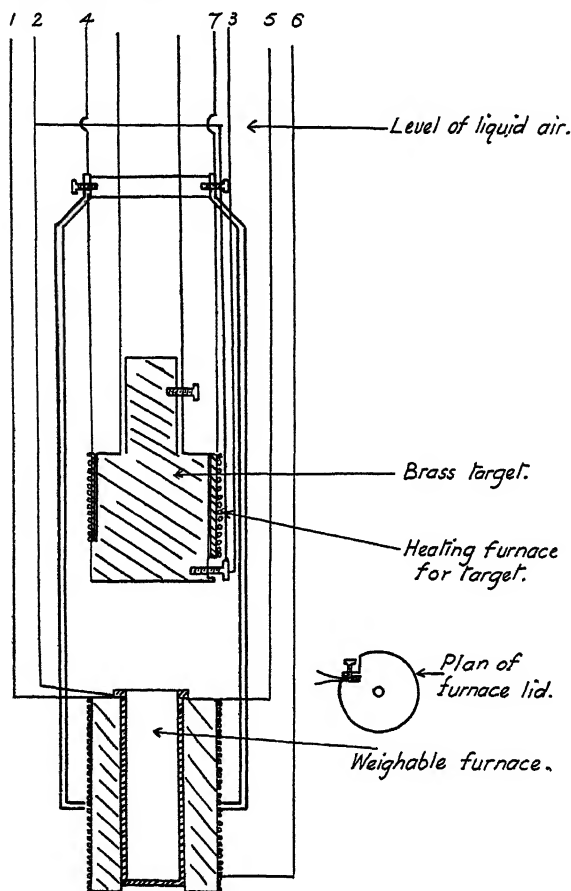


FIG. 1.

Key to terminals. 1 and 2, thermocouples for furnace. 2 and 3, thermocouples for target. 4 and 7, to heating coil of target. 5 and 6, to heating coil of furnace.

lower rates of emission. All experiments on partial condensation were, however, made at stream densities of 0.1 mg./min. or higher and hence it is the properties of the stream under these conditions in which we are interested. The diameter of the orifice in these experiments was of the order of 1 mm., and the mean free path at the orifice was always small compared with 1 mm. On the other hand, when the molecules reached the target the mean free path had become large compared with 1 cm., and for this reason the deposit was confined to the front of the target and the various lead wires for the heating coils and thermocouples attached to the furnace gave sharp shadows on the walls of the outer tube. Experimentally it was

of a vapour reaching a cool enough surface will condense, and that for salicylic acid -40°C . is a low enough temperature for the stream densities used.

Experiments with a cold solid target could now be used to investigate the properties of the stream emitted by the furnace for salicylic acid. A series of 21 experiments were made at stream densities of 0.071 to 4.0 mg./min. on the surface area of the target, and the fraction of the molecules leaving the furnace which struck the target was found to be constant and equal to 0.234. A series of five experiments carried out at a stream density below 0.03 mg./min. gave a lower value of 0.224. For a cosine distribution of the molecules striking the target should be 0.200, hence we may assume that this lower value indicated a tendency to a cosine distribution at the

found that the constancy of the fraction striking the target over a range of stream densities was characteristic of iodine, stannic iodide and mercuric iodide as well as salicylic acid, and only anthracene gave a variable ratio. Finally, it was possible to give a rough quantitative explanation of the constancy of the ratio with the aid of the following assumptions:—

(1) That the point of narrowest cross section of the jet emitted by the furnace is near to the orifice. Hydrodynamic theory⁵ indicates that the velocity of efflux is here equal to the velocity of sound in the vapour under the same conditions of temperature and pressure.

(2) That the distance which a molecule had to travel from the orifice before the mean free path became so long that the effects due to collision between the molecules in the stream could be neglected, was so short that it could be assumed that this condition was fulfilled at the orifice itself.

(3) That the distribution of velocities was a Maxwellian one, with superimposed on it a velocity equal to the velocity of sound in the direction of the stream.

With these assumptions the probability that a molecule with a given thermal velocity would have a resultant velocity in such a direction that it would strike the target could be calculated. This probability was then summed over a Maxwellian distribution curve and the ratio of the area of the curve so obtained to the area of the original Maxwellian curve gave the fraction of the molecules striking the target.*

This calculation was carried out in the case of iodine and the result obtained was that the fraction of the molecules striking the target should be independent of the stream density and equal to 0.233. The experimental value was 0.230. Here the agreement is much closer than the approximations in the calculations would lead one to expect; it should be noted that the only property of the substance that is important in the above calculations is γ (the ratio of the specific heats). In the case of iodine γ was taken as 1.30, for salicylic acid, however, we should expect that $\gamma = 1.10$ and in this case the ratio striking the target should be 0.220 as compared with the experimental value 0.234. This method of calculation always gives values to the ratio which are constant with stream density and, in accordance with the experimental results higher than that given by the cosine distribution, a fact which gives support to our general picture of the nature of the stream emitted by the orifice. In the case of anthracene, however, the fraction striking the target varied from 0.290 at 0.2 mg./min. to 0.230 at 3 mg./min., these results were not so easily reproducible as with the other substances, but the variation with stream density was always there. It should be noted that in the case of anthracene the molecular weight is of the same order as those of the other substances used but the collision area is much larger; we should therefore expect that collisions in the stream would be more important with anthracene than with the other molecules. Scattering in the beam would account for the decrease in the fraction of molecules striking the target at high stream densities, but the explanation of the high value of 0.290 is not clear.

All these experiments on the fraction of molecules striking the target were made with the target at a sufficiently low temperature to ensure the complete condensation of all the incident molecules.

⁵ Lamb, *Hydrodynamics*, p. 25.

* A correction had to be applied for the molecules with a resultant downward velocity. For these molecules it could be assumed either that they are not emitted by the furnace and their number subtracted from the stream, or that in reality they move downwards from a point above the orifice so as to strike the lid of the furnace and to be reflected upwards with a cosine distribution. In the case of iodine these two assumptions give the results of 0.235 and 0.231. respectively, so that the difference is unimportant from the present point of view.

Both furnace and target were fitted with heating coils and thermocouples, and with the aid of these it was possible not only to vary the rate of emission of the furnace but also to make measurements at higher temperatures where complete condensation of all incident molecules did not occur. Such measurements were made in the following way:

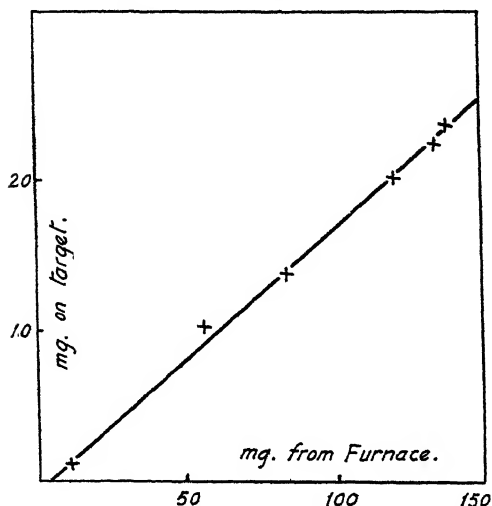


FIG. 2.—Deposition on target against emission of furnace for salicylic acid. Temperature of target $+7^{\circ}\text{C.}$, furnace 106°C.

The target was heated to its appropriate temperature and the apparatus evacuated, the furnace was then heated to the correct temperature, the experiment continued for a suitable period and then stopped by admitting air into the apparatus. A series of experiments for different times but with the same temperature of furnace and target yielded a series of measurements of the deposition of the target all at the same stream density, and from these a curve could be plotted showing the weight deposited on the target as a function of the weight emitted by the furnace as shown in Fig. 2. The relationship obtained was, as would be expected, linear,

but the line did not go through the origin; one reason for this was that the deposition of the first layers on the target did not proceed so smoothly as the subsequent deposition, and indeed it was sometimes necessary to cover the target with a thin deposit before making an experiment. This uncertainty at the beginning of the experiments did not

TABLE I.—EVAPORATION EXPERIMENTS WITH SALICYLIC ACID AT 7°C.

Weight (in mg.) on Target.		Time (min.).	Rate of Evaporation mg./min.
Before Expt.	After Expt.		
22.3	13.2	110	0.083
20.3	6.05	135	0.105
14.3	8.9	56	0.096
6.2	4.1	25	0.084
Average $E = 0.092\text{mg./min.}$			

effect the results since they were always obtained from the slopes of these lines, which divided by 0.234 (in the case of salicylic acid), give the ratio D/ν where D was the rate of collection on the target in mg./min.^{-1} and ν was the amount falling on the target also in mg./min.^{-1} . In all cases these quantities were calculated for the whole area of the target, *i.e.* $\pi \times 1.25^2 = 4.9\text{ cm.}^2$ and mg./min.^{-1} and they could be reduced to $\text{mg./min.}^{-1}\text{ cm.}^{-2}$ by dividing by 4.9. Therefore ν could be regarded as a measure of the stream density; it was always obtained from the average of the stream densities of the points constituting a graph such as that shown in Fig. 2.

In addition to these experiments, measurements were also made of the rate of evaporation of a deposit into a vacuum by finding the loss of mass from the target in a definite time. A series of results for this type of experiment is shown in Table I, and the average of several experiments

will give E the normal rate of evaporation of a deposit in mg./min. for a target of diameter 2.50 cm.

The estimation of the deposits, which were of the order of 10 mg., was made by titrating in the case of salicylic acid and iodine; for the other substances a target with a removable lid was used and the deposits were weighed.

It will be seen that the measurements above yielded three quantities at a given stream density and temperature (D , v , and E). It was convenient to define a quantity A , which was called the adhesion ratio, by the relation

$$A = \frac{D + E}{v}.$$

This adhesion ratio had no direct theoretical significance, but it is a measure of the difficulty of transition from vapour to crystal phase. A high adhesion ratio means that an incident molecule stands a small chance of re-evaporation before it is attached to the lattice or is adsorbed in an energy position not greatly differing from that of a molecule in the lattice.

Experimental Results.

In Fig. 3 the adhesion ratios of a number of substances are plotted against $\log E$. As E is approximately exponential with temperature, its logarithm serves as an approximate temperature scale for each substance, and for comparing different substances it is more convenient to use a scale of $\log E$ than a scale of temperature. It will be seen from this figure that as $\log E$ decreases $A \rightarrow 1$, and that further, the probability that a molecule striking a crystal surface will fail to condense there does not become appreciable until the probability that a molecule fixed in the crystal lattice will evaporate into the gas phase becomes measurable. The figure does not show the

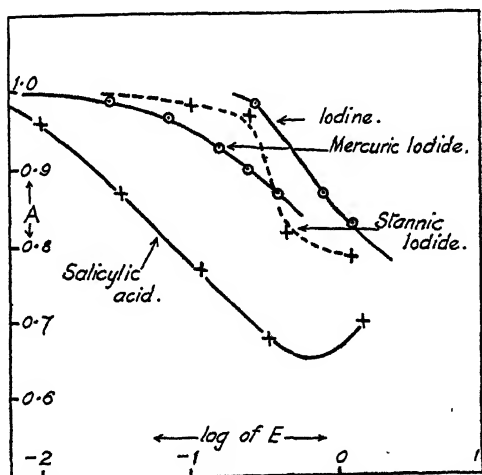


FIG. 3.—Adhesion ratios A plotted against the logarithm of the rate of Evaporation E .

total range temperature variation over which the measurements were made, but it varied between 8° C. for iodine and 30° C. for salicylic acid, and within a temperature range of this order A always rises sharply to unity from fractional values; this suggests that neither reflection nor elastic collisions with molecules on the crystal surface play an important part in the mechanism of crystal growth. We should hardly expect that either of these processes would be sharply dependent on the temperature of the condensing surface, and it is clear that neither of them can occur at temperatures only slightly below those at which the condensation experiments were made. This evidence is in accordance with the views that have been expressed by

others, e.g. Eucken,⁶ who considered that spectral reflection does not occur from crystal surfaces since the reflected streams are always diffuse. It is assumed in the subsequent discussion that all the molecules striking the surface of a growing crystal are adsorbed in one way or another though they may not necessarily be attached to their appropriate place in the crystal lattice.

Salicylic Acid.

It will be seen from Fig. 3 that, of all the substances used, salicylic acid shows the smallest values of A and in particular that with it the fall in A occurs at much smaller values of E than with other substances. Now, only experiments made where A is less than unity are of interest: also if ν becomes of the same magnitude as E , condensation may cease and evaporation set in, hence in this region steady deposition experiments cannot be made; in general the best results are obtained when ν is large

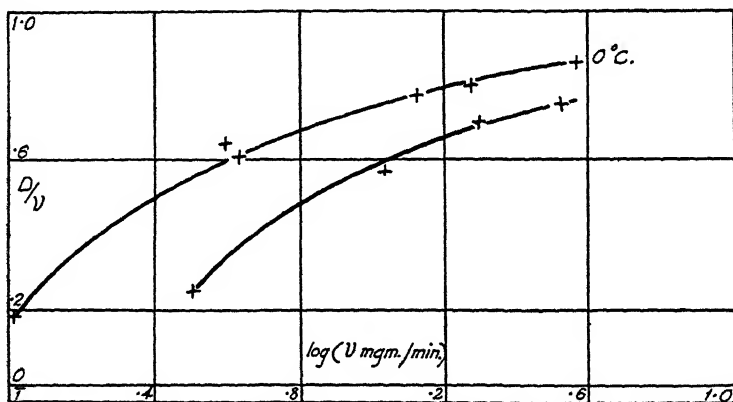


FIG. 4.—Variation of D/ν with stream density (D).

compared with E . On the other hand, there is an upper limit in the neighbourhood of $\nu = 3$ mg./min. where the mean free path of the molecules at the target becomes of the order of 2 cm. and hence collisions between target and furnace can no longer be neglected; therefore the range of stream densities in which interesting experiments can be made is $\nu \sim 3$ mg./min. to $\nu \sim 2E$. If A does not fall below unity until temperatures are reached at which E is large then the range of stream densities at which experiments can be made is restricted. With salicylic acid, however, this difficulty hardly arises and experiments can be made at 0°C . with stream densities of 3.0 to 0.1 mg./min. in all of which partial deposition takes place. Also the temperature range over which measurements can be made is greater than for other substances.

The variation of D/ν with $\log \nu$ is shown in Fig. 4, and it will be seen that this ratio is not constant, as it would be if there were a constant condensation coefficient. An explanation of the variation of D with ν can be given in terms of the hypothesis of the existence of a mobile layer, but the relationships obtained between these two quantities can be more conveniently illustrated by other figures, which are shown with the theory that we now discuss.

⁶ Eucken, *Naturwiss.*, 1937, 14, 214.

Theory of Variations with Stream Density.—Crystals of salicylic acid growing under a microscope can be seen growing as needles almost entirely at their pointed ends. They grew into needles of a similar shape under experimental conditions, hence, if there was no surface mobility of molecules adsorbed on the crystal surface, the fraction of the incident molecules which could condense would be extremely low. However, the experimental results give values generally over one half; so that the assumption of surface mobility in an absorbed phase appears to be necessary. We may regard the growing face of the crystal as a number of fixed energy holes into which molecules can fall and out of which they can jump as a result of their vibrational energy. Let the concentration of mobile molecules (*i.e.* molecules not yet fixed in their final positions in the crystal lattice) on the growing face be c and the concentration on other crystal faces be proportional to c . Suppose these molecules react to give dimers, then the rate of formation of such dimers is $k \cdot c^2$.

Let the concentration of these dimers which can dissociate with an energy of dissociation Q be n . Then the rate of dissociation is given by $k'n e^{-Q/RT}$. Also if the crystal grows by the adhesion of dimers then rate of growth will be given by $k''n$. Therefore the equilibrium condition for dimers is

$$k \cdot c^2 = k'n \cdot e^{-Q/RT} + k''n.$$

If we now neglect $k''n$ which occurs only on the growing face in comparison with the other two processes which occur on all the faces we may write approximately,

$$n = \frac{k}{k'} c^2 \cdot e^{Q/RT}$$

and hence the rate of crystal growth is

$$K_1 c^2 e^{Q/RT}.$$

Here it is suggested that the dimerisation takes place in the mobile layer, but the same equation for the rate of growth is obtained if we assume, instead, that the formation of dimers takes place when the molecules attach themselves to the crystal surface. The essential point is that molecules in the mobile layer cannot start to behave as part of the crystal until they have been attached in pairs.

Therefore D = measured rate of deposition

= rate of growth — rate of loss from crystal

$$= K_1 c^2 e^{Q/RT} - K_2 e^{-X/RT} - K_3 e^{-Y/RT} \quad (1)$$

where K_2 and X refer to the transition from a fixed position in the crystal lattice to the mobile layer, and K_3 and Y refer to the transition from a position in the lattice to the vapour directly.

On the other hand, since the concentration of mobile molecules on different crystal surfaces is assumed to be in a constant ratio, the rate of evaporation from the mobile layer and the crystal is given by:—

$$\nu - D = K_4 c e^{-Q'/RT} + K_3 e^{-Y/RT} \quad (2)$$

where Q' is the energy of absorption into the mobile layer of a molecule from the vapour. Now for salicylic acid at 0°C ., the rate of normal evaporation is only 0.03 mg./min. , hence the term $K_3 e^{-Y/RT}$ cannot be

greater than this and actually should be much less. Also Neuman ⁷ has shown theoretically that if a mobile layer plays a part in crystal growth then very few molecules will pass directly into the vapour phase without first passing through the mobile layer.

If we neglect this direct transition from the crystal to the vapour then, by eliminating c , the concentration in the mobile layer about which we know little, the relationships (1) and (2) can be reduced to the form

$$D = k_1(\nu - D)^2 \cdot e^{\frac{Q + 2Q'}{RT}} - k_2 e^{-X/RT}. \quad (3)$$

This is a theoretical equation describing the growth of crystals of salicylic acid.

Equation (3) can now be applied to the experimental results. If we take the values of D at different stream densities for the two temperatures

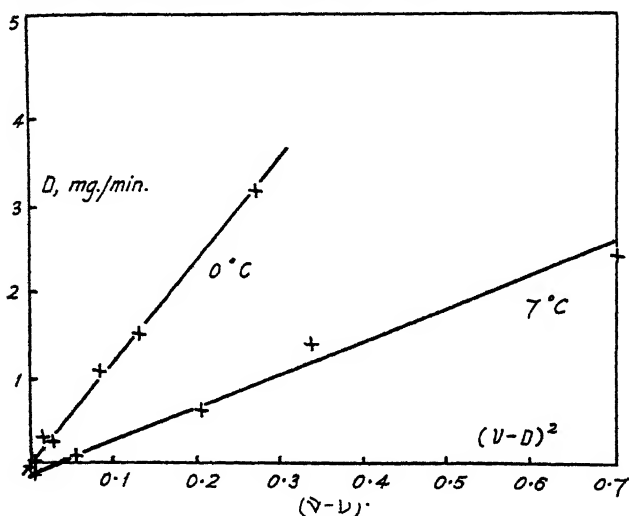


Fig. 5.—Graph of D against $(\nu - D)^2$ for salicylic acid at 0°C and 7°C .

0°C . and 7°C . we can plot D against $(\nu - D)^2$ and so get the two straight lines shown in Fig. 5 in which the points for $\nu = 0$, i.e. when $D = -E$, are included.

The fact that straight lines can be obtained in this way shows once again that any attempt to describe the condensation of salicylic acid in terms of a single condensation coefficient is unsatisfactory. In fact the condensation coefficient f as defined by Alty ⁴ can be expressed in terms of the above symbols as $f = E/\nu_{\text{eq}}$ where ν_{eq} is the stream density falling on a crystal surface that is surrounded by its vapour at equilibrium. The values of f so obtained (at 0°C : 0.54 ; at 7°C : 0.56) are less than unity though rather higher than the value of 0.29 found by Alty in the case of benzoic acid.

From the ratio of the slopes of the lines at 0°C . and at 7°C . we obtain $Q + 2Q' = 22,900$ and from the intercepts* on the D axis we get

⁷ Neuman, *Z. Elektrochem.*, 1938, 44, 474.

* The ratio of the intercepts is, of course, not so accurate as the ratio of the slopes, but it can be obtained much more accurately than Fig. 5 would suggest by plotting out the points nearest to the origin on a larger scale. The percentage errors do not vary very greatly over the different points on these lines.

$X = 24.000$ cal. Since X refers to the energy of transition from a fixed point in the lattice to the mobile layer we should expect it to be less than the latent heat of sublimation; actually it is rather greater since the latent heat is measured by Hirsbrunner⁸ is only 19.500 cal. This is probably due to the molecules jumping from the lattice into the mobile layer in pairs.

The Variation with Temperature.—All the experimental evidence in support of equation (3) has so far been taken from measurements of the condensation of salicylic acid at different stream densities at the two temperatures of 0° and 7° C. In addition to these results it is also possible to make experiments at other temperatures which give values of E and D/ν at a stream density of 3 mg./min., and hence we can derive values of A at these other temperatures. Such a curve showing the variation of A with temperature is plotted in Fig. 6, curve I. If we now make use of the energies of transition found from the measurements at 0° and 7° C. it is possible to calculate values of D at other temperatures

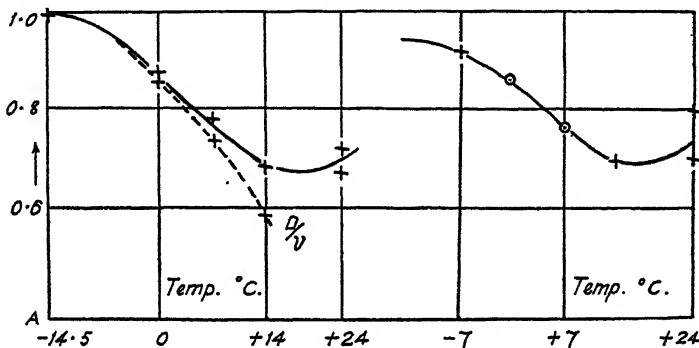


FIG. 6.—Adhesion ratio for salicylic acid against temperature.

Curve I.

Curve II.

Observed values with D/ν for comparison.

Calculated Curve.

and to obtain a calculated curve showing the variation of A with temperature (see Fig. 6, curve II), the two points at 0° and 7° C. being of course the same for curves I and II. The agreement between these two curves is not quantitatively accurate but they both have the same form. One interesting point may be noted: at 24° C. two experimental values of A were obtained, one near $\nu = 2$ mg./min. and the other near to $\nu = 4$ mg./min.; under these conditions it is the higher stream density which gives the lower value of A —quite the reverse of what occurs at lower temperatures; this reversal also occurs in the calculated points.

The Crystal Structure of Salicylic Acid.—These experimental results may be taken as supporting the bimolecular hypothesis as far as the growth of crystals of salicylic acid is concerned, and it seemed possible that some bimolecular arrangement would be present in the crystal structure. Salicylic acid was therefore examined by Mr. G. Knott of the Crystallographic Laboratory, Cambridge, who found, on the basis of a packing model, that the molecules were probably packed together in pairs as is common with other carboxylic acids. He also showed that these double molecules lay in planes inclined at an angle of 40–50° to the c axis. There were four molecules to the unit cell.

⁸ Hirsbrunner, *Helv. Chim. Acta*, 1934, 17, 477.

The Size and Shape of Crystals.—The crystals deposited on the target consisted of a felt of small needles, whose size was larger at high than at low temperatures. This is in agreement with the results obtained by G. Haas,⁹ who found that the size of crystals for deposits of silver and antimony was larger in the case of deposits formed at high temperatures than with those formed at low temperatures. In the case of the deposits of salicylic acid there was no well-defined variation of crystal size with stream density.

Finally, we may note that the growth of crystals of salicylic acid may be observed under a microscope with a hot stage arrangement and the growth takes place almost entirely at the ends of the needles, on a face inclined at an angle of approximately 40° to the long c axis. Under these conditions crystals 5 mm. long and $1/50$ mm. wide can easily be grown.

Mercuric Iodide.

This substance gave particularly satisfactory deposits in which the crystals were closely packed together and gave excellent microphotographs, from which three clear conclusions can be drawn.

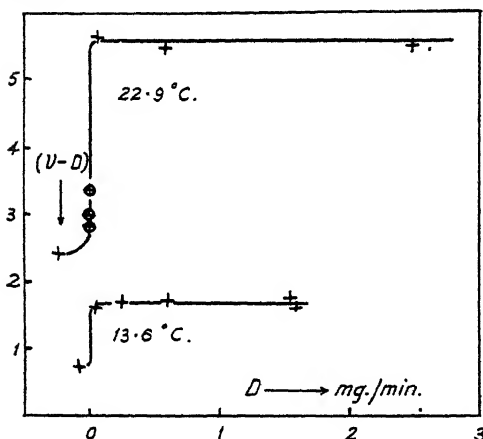


FIG. 7. — Isotherms of $(v - D)$ against D for mercuric iodide. The points marked \oplus are from single experiments and not from a series of experiments as described in text.

1. The crystals formed at higher temperatures are larger than those formed at lower temperatures.
2. There is a marked change in crystal size with stream density, the crystals formed at low stream density being much larger than those formed at a high stream density.
3. There is an effect whereby a deposit consisting of large crystals, when it is allowed to evaporate into a vacuum, as in the measurement of E , breaks up into very small crystals.

In the quantitative condensation experiments the ratio of the molecules striking the target was 0.220; however, the mercuric iodide had a tendency to react with the copper of the furnace lid to give a scale of mercuric iodide round the orifice and if this scale was allowed to accumulate then the ratio of the molecules striking the target had a tendency to rise. A reference to Fig. 3 will show that A falls below unity at a lower value of E than is the case with the other inorganic substances.

⁹ G. Haas, *Naturwiss.*, 1937, 232.

Here it is best to consider the changes in the number of molecules evaporating from the surface with changing stream density, *i.e.* the curve showing the variation of $(\nu - D)$ with D as is shown in Fig. 7. The characteristic aspect of these curves is that a certain value of $(\nu - D)$ must be reached if there is to be deposition and this quantity is not exceeded at high rates of deposition. This means that at a given temperature the deposition curve is influenced by two definite quantities, *vis.* E or $-D$ when $\nu = 0$, and $(\nu - D)$ for steady deposition. These two quantities can be plotted as a logarithmic curve against the reciprocal of the absolute temperature (see Fig. 8) and in this way two straight lines are obtained which correspond to energies of 22·500 and 20·400 cal. for E and $(\nu - D)$ respectively.* The heat of vaporisation of red mercuric iodide which was the form in which all the deposits occurred is given as 20·100 cal. by Shibata and Niwa;¹⁰ by extrapolating the vapour pressure measurements of these authors we can find the value of the

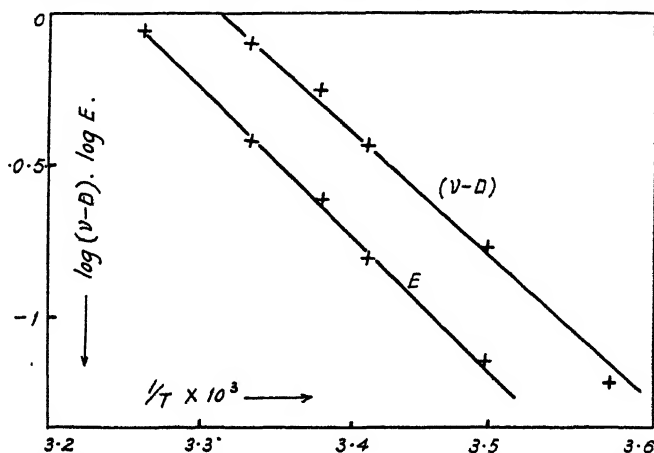


Fig. 8.—Logarithms of $(\nu - D)$ and E against the reciprocal of the absolute temperature of mercuric iodide.

Alty condensation coefficient for mercuric iodide, and at 27° C. this comes out at 0·61 and is thus in agreement with the value of 0·53 obtained by Metzger and Miescher.¹¹ This shows us that the vapour pressure curve cuts the vertical part of the D , $(\nu - D)$ curves shown in Fig. 7 near the top, in this case therefore we should expect that a crystal of mercuric iodide should grow steadily in its supersaturated vapour. This was shown to be the case by some experiments similar to those carried out by Volmer and Schultze¹² which showed that a crystal of mercuric

* A possible explanation of the above phenomena would be that the molecules striking a crystal of red HgI_2 go through a surface phase similar to the unstable yellow form. If this was so, then we should expect that the two lines should cut at a temperature of 127° C. the transition point of red to yellow mercuric iodide. Actually they cut at 110° C. and the difference between this temperature and the transition point is well within the experimental error. The disadvantage of this view is that the ratio $(\nu - D)/E$ is certainly above 2 at 27° C. and this requires an energy difference of 2·000 cal. if the two are to be the same at 127° C.; the heat of transition of red to yellow mercuric iodide is only 600 cal. (Steiner and Johnson, *J. Physic. Chem.*, 1928, 32, 912).

¹⁰ Shibata and Niwa, *J. Sci. Hokkaido Univ.*, 1938, 3, 183.

¹¹ Metzger and Miescher, *Nature*, 1938, 572.

¹² Volmer and Schultze, *Z. physik. Chem.*, 1931, 156.

iodide could grow steadily in its vapour which was supersaturated to the extent of 0.43°C ., the experiments being made at a temperature of 100°C .

Anthracene.

Some experiments were also carried out on anthracene, which yielded D , $(\nu - D)$ curves of exactly the same type as those shown in Fig. 7. In the case of anthracene the ratio of $(\nu - D)/E$ for the maximum value of $(\nu - D)$ was near to 3 instead of 2 as is the case with mercuric iodide, and consequently anthracene gave lower values of A than did mercuric iodide. The energies obtained from two such curves for anthracene were within the experimental error equal to 17.000 cal ., the heat of sublimation.

Discussion of the Experiments on Mercuric Iodide and Anthracene.

The interpretation of these experimental results is open to considerable doubt, and it is probable that the results by themselves are not sufficient to form the basis of a complete theory. It is, however, possible to explain them if we assume that thick layers of disarranged molecules are built up on the surface of a crystal on which deposition is taking place. As soon as these layers become thick any increase in the stream density does not affect the condition of the surface or the rate at which molecules will evaporate from it; on the other hand, when a crystal is evaporating the surface exposed to the vacuum is not covered by these thick disarranged layers and consequently the rate at which molecules are given off is lower. A thick layer hypothesis will also cover the decrease in crystal size with increasing stream density observed with mercuric iodide, since at high stream densities the layers will be thicker and consequently the chances that a new crystal germ will be formed will be greater for a given area of crystal surface than would be the case for a thinner layer.

Stannic Iodide and Iodine.

The fraction of molecules striking the target was for iodine 0.230 (average of 30 experiments) and for stannic iodide 0.234 (average of 7 experiments).

The curves showing the variation of A with $\log E$ for these substances are shown in Fig. 3. It will be seen at once that in these cases A does not start to fall appreciably below unity until very high values of E are reached. To put this in another way, the number of vapour molecules leaving a crystal surface is hardly increased when deposition takes place. This is best shown by comparing the figure of $(\nu - D)$ at $\nu = 3\text{ mg./min.}$ with the measurements of E .

In the case of iodine we have:—

	$- 44.4^{\circ}\text{C.}$	$- 46.8^{\circ}\text{C.}$	$- 52.6^{\circ}\text{C.}$
$(\nu - D)$	1.62	1.17	0.28 mg./min.
E	1.23	0.87	0.27 mg./min.

Since the technique of the experiment is essentially based on the measurement of differences in $(\nu - D)$, few definite conclusions can be drawn when no considerable variations in $(\nu - D)$ can be recorded.

With stannic iodide measurements were carried out at two different stream densities at a temperature of 7° C.

ν	$D (-E)$	$(\nu - D)$
2.60	2.28	0.32 mg./min.
0.51	0.21	0.29 "
0	0.25	0.25 "

The fact that the number of molecules evaporating from the crystal surface is almost invariant with stream density suggests that a molecule striking the crystal surface is quickly adsorbed in a position where its energy state is much the same as that of a molecule attached to the lattice. This may be connected with the symmetrical character of the iodine and stannic iodide molecules, the result of which is that though these molecules may behave in a similar way to mercuric iodide and anthracene, they are able to arrange themselves much more easily into positions appropriate to the crystal lattice.

Summary.

Measurements are made on the rate of growth of a crystal mass from a vapour stream of known density. It is shown that in no case can the results be explained on the basis of a constant condensation coefficient. With salicylic acid the experiments are explained by a bimolecular process occurring in a mobile surface phase and this is in agreement with the crystal structure. Measurements are also made with mercuric iodide, anthracene, iodine and stannic iodide, and the results obtained with these substances suggest that thick layers of disarranged molecules may be built up on the surface of growing crystals.

I am indebted to the Salters Company for a Fellowship, to the Department of Scientific and Industrial Research for a grant, and to Professor E. K. Rideal and Dr. J. K. Roberts for many helpful discussions during the progress of this work.

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A NEW METHOD OF SPREADING MONOLAYERS OF ALBUMIN AND LIPOID-ALBUMIN MIXTURES.

BY STINA STÄLLBERG AND TORSTEN TEORELL.

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Several workers on protein monolayers have clearly shown that a complete and rapid spreading may be difficult to achieve. Many factors seem to be involved, such as the pH and concentration of the spreading solution, the electrolyte concentration and pH in the substrate, etc. (an extensive survey has recently been published by Neurath and Bull.¹) It appeared to us that the difficulties were partly due to the fact that the proteins were spread either from an aqueous solution or from the solid.

¹ H. Neurath and H. B. Bull, *Chemical Reviews*, 1938, 23, 391. Cf. also G. Th. Philipp: *On the Nature of Proteins*, Thesis, University of Leiden, 1936 (pH and salt effects); J. S. Mitchell, *Trans. Faraday Soc.*, 1937, 33, 1129 (protein concentration effect). I. Langmuir and V. J. Schaefer, *Chem. Rev.*, 1939, 27, 181.

Special proteins, like gliadin, which are soluble in ethyl alcohol, seemed to spread quite well from alcoholic solution, probably because this solvent remains more readily on the surface and spreads out faster and more uniformly than an aqueous solution would do. An attempt was therefore made to see if other proteins could be brought into a uniform solution in a suitable non-aqueous medium. Examination was limited to such liquids as can also dissolve lipoids, since thereby a method would arise for spreading *mixed* lipo-protein films. Mixed films of proteins with lipoids have been but little investigated so far, in spite of the obvious significance such films offer in connection with many biological problems,² apparently for lack of a suitable solvent.

After various trials a suitable solvent was found to be a propyl alcohol-sodium acetate mixture. The composition is based upon previous observations by one of us³ on the influence of alcohols and acetate salt upon the solubility of albumins. This solvent exhibits the following features: (a) it can dissolve albumin to a clear solution which keeps indefinitely, (b) it can also dissolve lipoids like cholesterol, lecithin, etc., (c) it can be heated to boiling without precipitating the protein—this boiling brings about true heat-denaturation as will be shown in a subsequent paper⁴—(d) it has excellent film-spreading properties both at the air/water and benzene/water interfaces (*cf.* Alexander and Teorell⁵).

Procedure.

In a small flask is mixed 3 c.c. of 1.7 M. Na-acetate and 6 c.c. of pure propyl alcohol, and then with vigorous stirring is added 1 c.c. of an aqueous protein-solution (containing ca. 1-10 mg./c.c.). Often a slight opalescence appears, which after a few hours leads to a small precipitate. This appears to be denatured protein and should be filtered off. (The maximum loss is about 10 per cent., generally far less.) The filtrate is usually perfectly clear and can remain unchanged indefinitely even at room temperature. This loss necessitates a separate micro nitrogen determination of the filtrate in order to obtain the final protein concentration. Both normal and *iso*-propyl alcohol can be employed. This procedure works well for serum albumin and gliadin, egg albumin is sometimes too easily denatured and frequently gives instable solutions. In such cases addition of strong HCl to a distinctly acid reaction (thymol blue reddish) is beneficial.

Mixed protein solutions with cholesterol, phosphatides, etc., are most easily made by dissolving the lipid substance (ca. 5 mg.) in the 6 c.c. portion of the propyl alcohol before adding the protein. The presence of the lipid does not seem to interfere with the solubility of the protein. Alternatively solutions of the protein and lipid (both in the 60 per cent. alcohol-acetate mixture) can be mixed in suitable proportions.

The actual spreading is performed by the aid of an "Agla"-micrometer syringe, either by dropping, or preferably by inserting the tip of the needle just in the interface.

Discussion.

The important point in connection with this new spreading technique is to prove that the protein in the propyl alcohol-Na acetate mixture exists

² J. H. Schulman and E. K. Rideal have investigated the ethyl alcohol soluble plant protein gliadin in mixtures with cholesterol (*Proc. Roy. Soc., B*, 1937, **122**, 29; *cf.* also J. H. Schulman, *Trans. Faraday Soc.*, 1937, **33**, 1116; H. Neurath (*J. Physic. Chem.*, 1938, **42**, 39) has used a simultaneous spreading of egg albumin + myristic acid.

³ T. Teorell, *Biochem. Z.*, 1930, **229**, 1.

⁴ S. Stållberg, *this journal*, see subsequent paper.

⁵ A. E. Alexander and T. Teorell, *Trans. Faraday Soc.*, 1939, **35**, 727.

in such a state that it gives surface films with the same properties as when spread by the usual methods. For that purpose the following arguments can be put forward:

(a) The bulk protein molecules did not seem to be changed in regard to their water-solubility since after dialysing away the propyl alcohol-Na acetate no precipitation occurred (in contrast to a solution denatured by heat, *cf.* the subsequent paper by Ställberg⁴). Also the salting-out properties with salts (*e.g.*, Am_2SO_4) had not been affected.

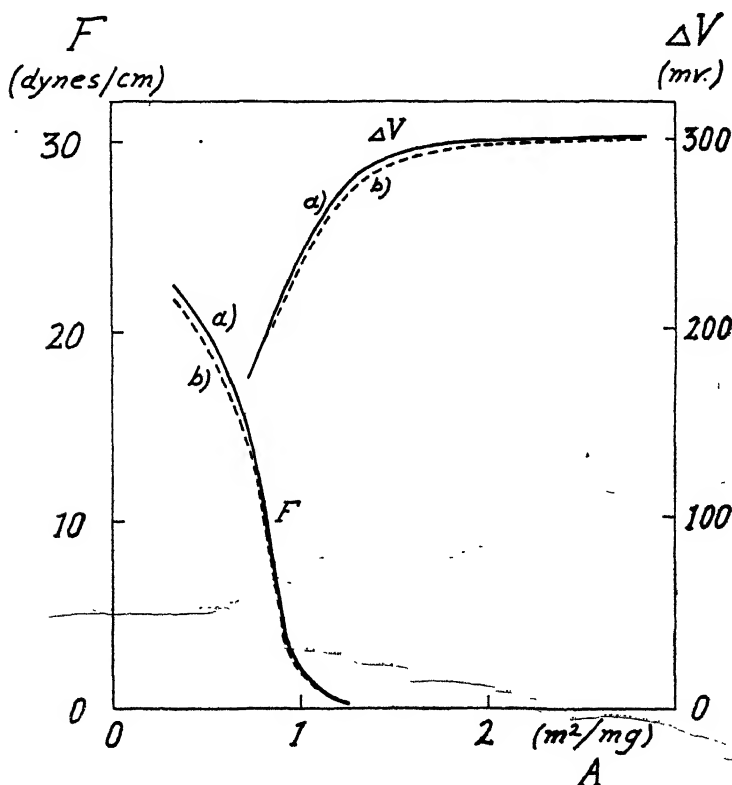


FIG. 1.—A comparison of surface films of serum albumin spread from (a) propyl alcohol-Na acetate mixture and (b) 0.15 M. NaCl. The protein concentrations were of the order 0.4 mg./c.c. The substrate was 0.15 M. NaCl buffered to pH 7 by M./150 phosphate mixture. For ΔV read the abscissa as $1/A$ mg./m.²

(b) The nitroprusside test for SH was negative.

(c) The electrophoretic mobility of the protein of the dialysate (as tested by the Tiselius technique) was identical with the same "native" protein.

(d) Monolayers spread from the propyl alcohol-Na acetate solution gave force-area and surface-potential curves identical with those spread from a purely aqueous solution (0.15 M. NaCl), when spread on the same substrate, see Fig. 1. The "zero compression areas" were in both cases practically the accepted standard value (ca. 1 m.²/mg.). This was true for serum albumin in particular. With egg albumin deviations

were frequently found, but the employment of an acid-spreading solution (as suggested by Bull ⁶) improved the results.

Hence it would seem, as far as can be judged at present, that albumin films spread according to the new procedure are identical with those obtained from the "native" protein.

The behaviour of mixed lipid-albumin films will be discussed in a forthcoming publication, but it may be mentioned that such films reveal several interesting properties, for instance, they can often withstand much higher compression than either of the components alone. The "expelling effect" discovered by Schulman and Rideal ⁷ with gliadin-cholesterol films has also been found with albumin-cholesterol and albumin-phosphatide films (at high compression, liquefaction of these films was observed).

Summary.

A 60 per cent. aqueous solution of propyl alcohol (normal or *iso*-) containing 0.5 molar Na-acetate has been employed as a solvent for both albumin and lipoids. Such a solution can be used for spreading monolayers of albumins, lipoids or mixtures thereof.

The expenses of this research were defrayed by the Rockefeller Foundation and by the Therese and Johan Andersson Foundation.

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⁶ H. B. Bull, *J. Biol. Chem.*, 1938, **125**, 585.

⁷ J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., B*, 1937, **122**, 29.

SURFACE FILMS OF HEAT-DENATURED SERUM ALBUMIN.

BY STINA STÄLLBERG.

Received 9th August, 1939.

During recent years surface layers of proteins have been rather extensively studied (for a review see Neurath and Bull ¹). Some attempts have also been made to reveal the structural changes which proteins undergo when subject to denaturation. It has long been known that *bulk* molecules are radically changed during heat-denaturation ^{2, 3} shown for example by increased viscosity. Neurath and Saum ⁴ have recently found a similar change with serum albumin which they attribute to an elongation of the originally approximately spherical molecule. Mirsky and Anson ⁵ have demonstrated that chemical changes occur

¹ H. Neurath and H. B. Bull, *Chemical Reviews*, 1938, **23**, 396.

² W. Y. Loughlin, *Biochem. J.*, 1933, **27**, 97.

³ W. C. M. Lewis, *Chemical Reviews*, 1931, **8**, 81.

⁴ H. Neurath and A. M. Saum, *J. Biol. Chem.*, 1939, **128**, 347.

⁵ A. E. Mirsky and M. L. Anson, *J. Gen. Physiol.*, 1936, **19**, 427.

during denaturations, for example —S—S— groups transformed into —SH. As the bulk molecules appear to be markedly rearranged, one might also anticipate that denatured protein in the form of a monolayer would show differences from films of native protein. Elaborate studies by Bull⁶ have, however, failed to demonstrate any significant differences in the molecular areas and compressibilities between monolayers of native and heat- or urea-denatured egg albumin, suggesting that the spread and denatured forms are structurally very similar.

Bull used egg albumin in his studies but apparently had difficulty in spreading the denatured product, which necessitated the use of a rather acid spreading solution (pH 2.2). In all cases the "zero compression" areas of the denatured were less than those of the "native" protein (see his Fig. 1 on p. 589). The author has also found that egg albumin spreads rather badly, so the suspicion arose that Bull's denatured films were never completely spread. The properties of monolayers of "native" and heat-denatured proteins have therefore been re-investigated according to a somewhat different mode, using the more easily-spreading serum albumin in combination with a new "spreading solvent" (cf. Stållberg and Teorell⁷). Surface potential measurements have also been performed in order to obtain possible information as to any polar group alterations or rearrangements.

The results given below indicate that a protein film can undergo a further expansion after heat-treatment in contrast to Bull's findings, whereas the difference in the apparent electrical dipole moment appears to be insignificant.

Technique.

The *stock serum albumin* was electrophoretically uniform and was prepared from human serum by the Tiselius⁸ electrophoresis method. It was found that samples from different sources varied but slightly.

The *spreading solutions* were made up in 60 per cent. *n*-propyl alcohol containing 0.5 M. sodium-acetate. The final protein concentration was 0.02-0.05 per cent. The employment of this propyl alcohol-acetate mixture is based upon previous work^{9a} showing that this mixture greatly aids complete and rapid spreading. Also it has the advantage that it can keep the heat-denatured protein in solution,^{9b} thus enabling spreading, even of this, to be easily achieved. *Heat-denatured* films were spread from the same solutions after heating for 30 minutes in sealed-off glass tubes in a water bath at 100° C. Thus a strict comparison was possible between unheated and heated protein solutions. The criteria showing that this treatment yields a denatured product are given below in the discussion. Spreading was performed by the aid of an "Aglä"-micrometer syringe.

The *substrate* upon which the films were spread contained a high salt concentration (0.15 M. NaCl) to assist spreading.¹⁰ The pH was 7.0 (M./150 phosphate) and the temperature about 20° C.

The *surface balance* and *surface potentiometer* was of a construction similar to that employed by Schulman and Rideal.¹¹

⁶ H. B. Bull, (a) *J. Biol. Chem.*, 1938, **125**, 585; (b) *Cold Spring Harbor Symposia on Quantitative Biology*, 1938, vi, 140.

⁷ S. Stållberg and T. Teorell, see preceding paper.

⁸ A. Tiselius, *Trans. Faraday Soc.*, 1937, **33**, 524.

⁹ (a) S. Stållberg and T. Teorell, *this Journal*, see preceding paper; (b) T. Teorell, *Biochem. Z.*, 1930, **229**, 1.

¹⁰ Cf. for instance G. T. Philippi: *On the Nature of Proteins*, Thesis, Leiden, 1936, p. 47.

¹¹ J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., A*, 1931, **130**, 259.

Results.

For each set of conditions from five to eight single experiments were performed. The mean of these was calculated and is plotted a smooth curve in Fig. 1, as the usual force-area (F/A), surface potential-surface concentration ($\Delta V/n$) and apparent dipole moment-area (μ/A) relationships.

From the graph it can be inferred that after heat-denaturation films of serum albumin:

(a) Are definitely expanded as compared with those from "native" protein, the expansion being about 15 per cent. The "zero compression"

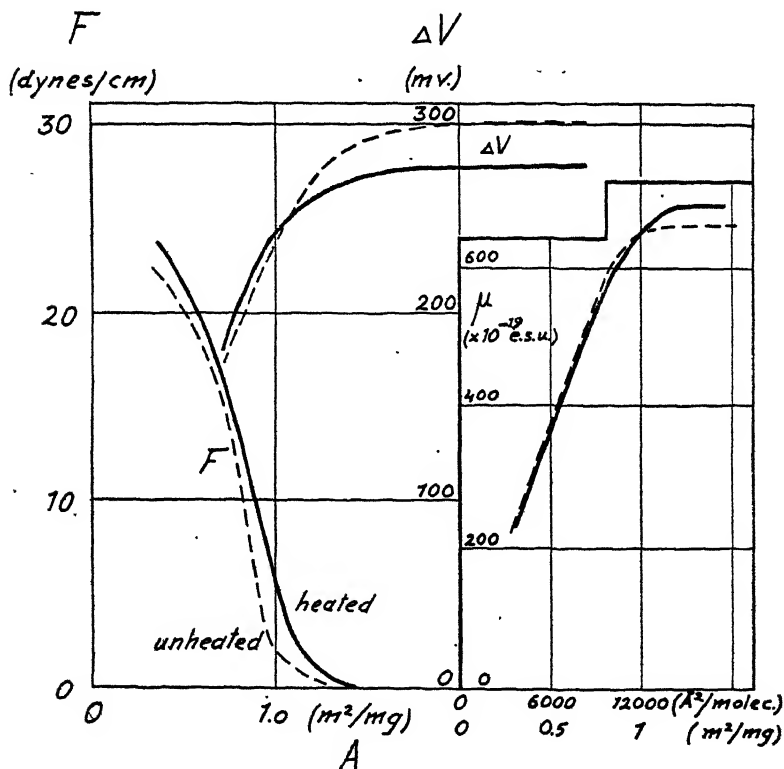


FIG. 1.—A comparison of surface film spread from unheated and heated solutions of serum albumin (ca. 0.4 mg. protein per c.c. of propyl alcohol-acetate mixture). Substrate: 0.15 M. NaCl at pH 7. Mwt. assumed to be 72-73,000. For ΔV read the left abscissa as $1/A$ mg./m.² which is proportional to the surface concentration n .

areas (which have usually been used for comparison purposes) are shown in Table I.

(b) Show a markedly increased compressibility (from 0.016 to 0.027 cm./dyne (Table I)). The figures were calculated from the slope of the middle linear portions of the F/A curves. In the range of high compression, however, it was always found that the heated protein showed a diminished compressibility.

(c) Have to be compressed to a higher pressure before a noticeable "gelation" was observed, although the corresponding areas seemed to be identical (Table I). The characterisation of the beginning of the "gel"

state is, however, a matter of some difficulty, so that the figures have only a relative value. In the high pressure region it was observed that the heat-denatured film never attained such a strong gel state as the "native" protein.

(d) Give a significantly lower value of the surface potential (ΔV) at high surface concentrations of the protein. When, however, the corresponding moments are calculated according to the usual formula $\Delta V = 4\pi \cdot n \cdot \mu$ (μ = apparent dipole moment, n = surface concentration) the differences are on the whole ruled out, and the values become nearly the same (*cf.* Fig. 1 and Table I).

TABLE I.—A COMPARISON BETWEEN "NATIVE" AND HEAT-DENATURED SERUM ALBUMIN (pH 7.0).

	Zero Com- pression Area.	Compressi- bility (Linear Portion).	Pressure (Area) at Beginning "Gelling."	Apparent Dipole Moment at Low Compression.
	m. ² /mg.	cm./dyne.	dynes/cm. (or m. ² /mg.).	milli-Debye.
"Native," NaCl-spread *	0.98	0.016	ca. 3 (0.95)	650
"Native," unheated .	0.99	0.016	ca. 6 (0.89)	649
Heat-denatured .	1.15	0.027	ca. 10 (0.89)	685

* Values quoted from ⁷.

Discussion.

In this investigation an apparently uniform protein species, serum albumin, has been spread as a monolayer before and after heating the spreading solution. As has been already pointed out (p. 1417), egg albumin is difficult to spread completely when denatured, which may explain why Bull, in contrast to our observed expansion of ca. 15 per cent., obtained a slightly more "condensed" *F-A* curve after denaturation. As the protein after heating in the propyl alcohol-sodium acetate mixture was evidently in a more highly dispersed state,¹² it might be argued that the heated protein should give a more completely spread film than the unheated. Against such a supposition stands, however, the following facts: Firstly, the unheated zero compression area was of the same order as found by other workers, *i.e.*, about one square meter per milligram, and further, was identical with that obtained by the standard spreading method with NaCl solution instead of the propyl alcohol mixture. Secondly, the heated protein curve gave a limiting area of 1.15 m.²/mg., which is far larger than the accepted standard area. Thus there is no doubt that the heated protein film presents a real expansion.

That this expansion is connected with a true denaturation is shown by the following experimental observations:

1. After dialysing away the propyl alcohol and sodium acetate the heated solution gave a bulky precipitate in contrast to the unheated, which only showed a slight opalescence. The precipitate could be redissolved in the above mixed solvent.
2. The heated solution alone gave a positive nitroprusside test¹³ indicating liberated —SH groups.

¹² A freshly made solution in general was slightly opalescent and gave, after 24 hours, a small precipitate (which was filtered off before using), whereas heating the fresh solution gave a perfectly and permanently clear solution.

¹³ S. W. Cole, *Practical Physiological Chemistry*, 9th ed., Cambridge, 1933, p. 124.

3. The viscosity measured by a Höppler viscosimeter at 25° C. increased after heating:

	<i>centipoise</i>
propyl-alcohol-acetate without protein . . .	4.65
unheated protein-propyl alcohol-acetate . . .	4.92
heated protein-propyl alcohol-acetate . . .	5.26

Hughes and Rideal¹⁴ suggested the fully extended β -keratin polypeptide chain structure in monolayers derived from native proteins, and Bull^{6a} supports a similar structure in those from denatured proteins. Since the evidence in favour of this view seems to be well-founded, it might appear somewhat difficult to understand the area expansions found in these experiments. However it can be reasonably suggested that this is a direct consequence of the chemical changes which have been shown to take place on denaturation (see p. 1417). Such changes have been shown to involve the breaking of certain bonds and the consequent liberation of new groups (in particular —S—S— being transformed to —SH HS—). The breakdown of such cross linkages would decrease the forces between the polypeptide chains and so permit a certain expansion of the film. The increase both in compressibility and in the gelation pressure seem to be consistent with this view. One apparent defect in this explanation is that such a change should be reflected in an alteration in μ , whereas no such change appears to take place. However, since the number of groups which undergo change during denaturation is small compared with the total number of polar groups, the change in moment may well be within the experimental error.

It can be concluded that, under the conditions here employed, monolayers from native and heat-denatured serum albumin differ appreciably, although much speculation as to the nature of this difference seems premature with our present knowledge of the architecture of the protein molecule.

Summary.

Surface films given by "native" and heat-denatured serum albumin have been investigated.

Denaturation was found to be accompanied by a marked increase in area (ca. 15 per cent.), changes in the compressibility, rigidity and the "gelation-point," but by no significant alteration in the apparent dipole moment.

I should like to thank Dr. A. E. Alexander for much kind advice and helpful discussions.

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¹⁴ A. H. Hughes and E. K. Rideal, *Proc. Roy. Soc., A*, 1932, 137, 62.

ON THE SOLUBILITY OF GASES. PART II.—A COMPARISON OF ORGANIC SOLVENTS WITH WATER.

By D. D. ELEY.

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1. Introduction.

In Part I¹ an attempt was made to understand the heats and entropies of solution of the inert gases in water, in terms of the force-fields involved and the statistical mechanics of a solution. In this paper a similar semi-empirical approach is made to the problem of organic solvents. In spite of the inevitable introduction of crude approximations, an insight into the factors involved can be gained, which may help to orient further experimental work. The lack of full and precise experimental data would exclude a rigid theoretical approach even if this were possible at the present time.

In this paper we concern ourselves mainly with the broad difference of behaviour that exists between water and organic solvents. A number of regularities have already been established for the solution of gases in organic solvents, *e.g.*, in the papers of Sisskind and Kasarnowsky,² Horiuti,^{3, 4} Körösy,⁵ and Uhlig,⁶ and these are in harmony with the views discussed here.

The characteristic feature of our treatment is to split the energy and entropy of solution into two parts:—

$$\begin{array}{llllll} \Delta E^0 = \Delta E_A + \Delta E_C & . & . & . & . & 1(a) \\ \Delta S^0 = \Delta S_A + \Delta S_C & . & . & . & . & 1(b) \end{array}$$

Here ΔE_C (ΔS_C) is the energy (entropy) change associated with the formation of a mole of cavities to accommodate the gas molecules. ΔE_A (ΔS_A) is then the energy (entropy) change occurring when a mole of gas is transferred from the gas phase to these cavities in the solvent. The symbol δ is used to denote the difference between one of these terms for water and for an organic solvent, *e.g.* $\delta\Delta E^0$ for He/Acetone/Water denotes the difference between the energy of solution of He in acetone and the energy of solution of He in water.

Unless otherwise stated, all data used are corrected to the standard states of Part I, *i.e.*, the gas at 1 atmosphere pressure in the gas phase, and at 1 mole per litre concentration in solution. The standard change in chemical potential of a gas on solution is then

$$-\Delta\mu^0 = RT \ln s - RT \ln 0.082T \quad . \quad . \quad . \quad (2)$$

where s is Ostwald's solubility coefficient. Also $-\Delta S^0 = \frac{\partial}{\partial T}(\Delta\mu^0)$ and

¹ Eley, *Trans. Faraday Soc.* This vol., p. 1281.

² Sisskind and Kasarnowsky, *Z. anorg. Chem.*, 1933, 214, 385.

³ Horiuti, *Sci. Pap. Inst. Phys. Chem. Research, Tokyo*, 1931, 17, 125.

⁴ Horiuti, *Z. Electrochem.*, 1933, 39, 20, 22.

⁵ Körösy, *Trans. Faraday Soc.*, 1937, 33, 416.

⁶ Uhlig, *J. Physical Chem.*, 1937, 41, 215.

$\Delta H^0 = -T^2 \frac{\partial}{\partial T} \left(\frac{\Delta \mu^0}{T} \right)$. The theoretical considerations are for these standard states.

2. Solutions of the Inert Gases.

We use the data of Lannung⁷ for organic solvents, and Valentiner⁸ for water. Lannung's data for water are in sufficient agreement with that of Valentiner to justify the following discussion. In Fig. 1a we

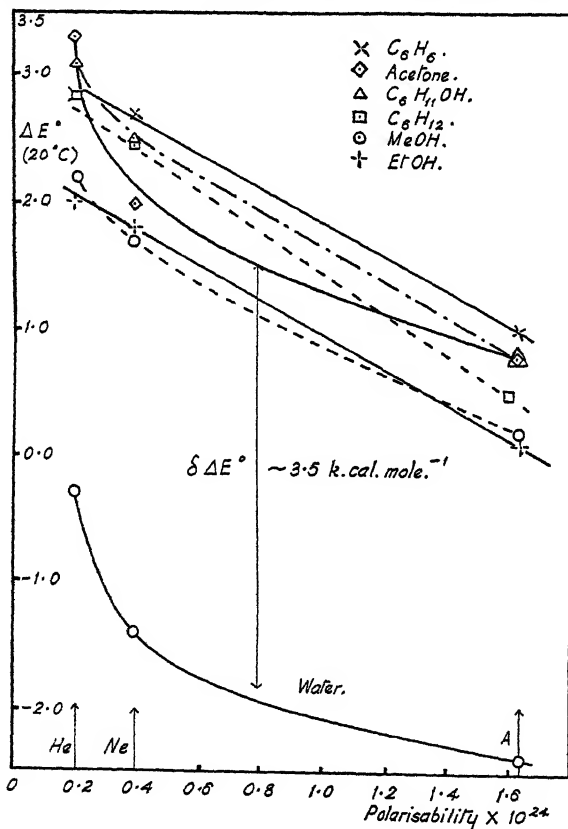


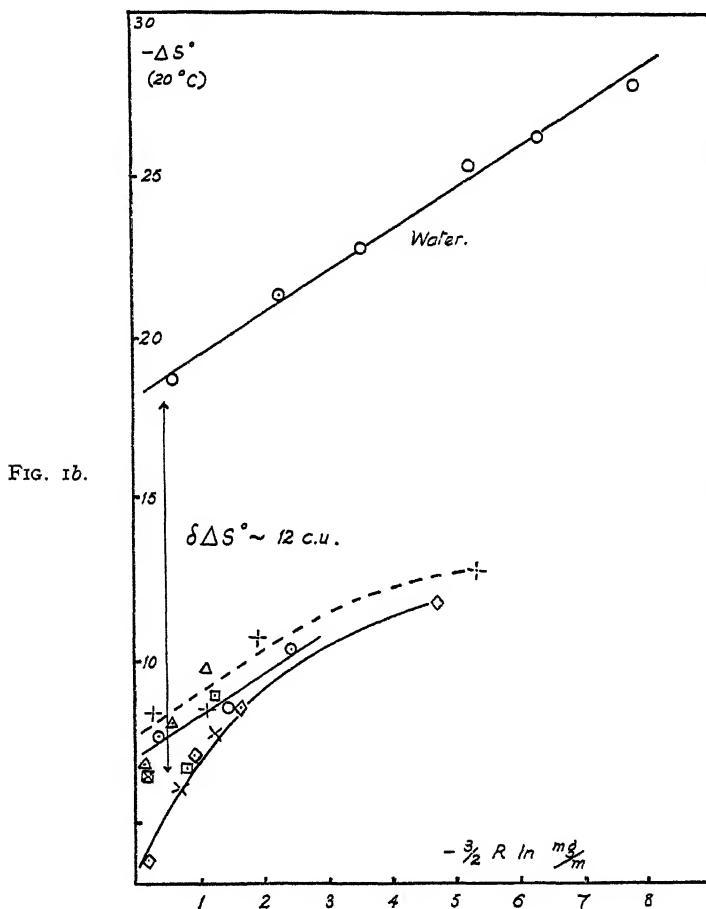
FIG. 1a.

plot the internal energy change for solution of the gas, $\Delta E^0 (= \Delta H^0 + RT)$ against the polarisability of the gas molecule. The differences between the individual organic solvents are too small to justify a detailed consideration; in some instances the fact that the curves cross each other may be due to experimental error. There is, however, a difference of roughly $3.5 \text{ k.cal. mole}^{-1}$ between ΔE^0 for a gas in an organic solvent, and ΔE^0 for the same gas in water, which we refer to as $\delta \Delta E^0$. We shall see that a large part of this difference is due to a difference in ΔE_C , $\delta \Delta E_C$, and that a given gas has much the same value of ΔE_A in all solvents, including water. We calculate ΔE_C as in Part I, $\Delta E_C = T(\alpha/\beta)\bar{V}$

⁷ Lannung, *J. Amer. Chem. Soc.*, 1930, **52**, 68.

⁸ Valentiner, *Z. Physik*, 1927, **42**, 253; *Landolt-Bornstein, Erg. IIa*, 479.

where α is the thermal expansion coefficient of the solvent, β its compressibility, and \bar{V} is the partial molal volume of the gas in the solvent. We take values of $T(\alpha/\beta)$ from Table III; since they do not vary much from one organic solvent to another one example, that of acetone, will suffice. \bar{V} for He/H₂O is 15 c.c., for He/Acetone we estimate it as 30 c.c. (see Table II). Then for He/Acetone/water $\delta\Delta E_G = 2.6$ k.cal. mole⁻¹, to be compared with the observed $\delta\Delta E^0$ of 3.6 k.cal. mole⁻¹. We have no data for \bar{V} for Ne and A, but in all cases we should expect values of



$\delta\Delta E_G$ of about 3.0 k.cal. mole⁻¹, to be compared with average value of $\delta\Delta E^0$ of 3.5 k.cal. mole⁻¹.

In a similar way we can explain the difference that exists between the entropy of solution of an inert gas in an organic solvent and in water. Fig. 1b shows this difference clearly. Here ΔS^0 is plotted against the variable $-\frac{3}{2} R \ln \frac{m_G}{m}$, where m is the mass of the gas molecule and m_G its reduced mass against a solvent molecule.

The average value of $\delta\Delta S^0$ is 12 e.u. (entropy units = cal. deg.⁻¹ mole⁻¹) and, since $T = 293^\circ \text{ K.}$, the equation $T\delta\Delta S^0 \sim \delta\Delta E^0$ roughly

holds. This relationship also holds for $\delta\Delta S_{\text{C}}$, since $\Delta S_{\text{C}} = (\alpha/\beta)\bar{V}$ as in Part I. For He/Acetone/water we have $\delta\Delta S_{\text{C}} = 8.9$ e.u., to compare with the observed $\delta\Delta S^0$ of 14.8 e.u. For the other gases and organic solvents values of $\delta\Delta S_{\text{C}}$ around 10.0 e.u. are to be expected. We conclude that ΔS_{A} for a given gas is much the same whether the solvent is water or an organic solvent. This is rather surprising, and is discussed in the next section.

3. The Partition Function for an Inert Gas in an Organic Solvent.

It is interesting to evaluate roughly the entropy of solution of an inert gas in an organic solvent, assuming that the partition function developed by Guggenheim is applicable.⁹ This partition function strictly applies only to an ideal solution of spherical molecules of equal size. In this instance the N_{G} gas molecules and the N_{S} solvent molecules ($N_{\text{S}} \gg N_{\text{G}}$) are to be regarded as interchangeable on $N_{\text{S}} + N_{\text{G}}$ quasi-lattice points, giving $(N_{\text{S}} + N_{\text{G}})! / N_{\text{S}}! N_{\text{G}}!$ distinct configurations. We can then derive equation (3) for the entropy of solution of a mole of gas, from equations 3(b), 7, and 13 of Part I.

$$\Delta S^0 = \Delta S_{\text{C}} + R \left[\ln \frac{N_{\text{S}} + N_{\text{G}}}{N_{\text{G}}} + \frac{3}{2} \ln \frac{m_{\text{G}}}{m} + \ln \frac{V_{\text{G}} N}{\bar{V}} + T \frac{\partial}{\partial T} \ln V_{\text{G}} - 1 \right] \quad (3)$$

V_{G} is the free volume of the gas molecule in solution, \bar{V}/N the volume per molecule in the gas phase (3.9×10^{-20} c.c.).

The term ΔS_{C} was introduced to account for all that part of the partial molal entropy of solution which arises from an alteration of the entropy of the solvent molecules, and so all restrictions on the solvent molecules in the field of the gas molecule are neglected. This is because the values of α and β used are those for the pure bulk solvent. The validity of this assumption is best examined by a consideration of ΔS^0 over the range He to A. For water, 50 per cent. of the observed variation in ΔS^0 can be accounted for by the variation in the mass factor $\frac{3}{2} R \ln \frac{m_{\text{G}}}{m}$, and the rest may be attributed to such neglected restrictions, which will increase as the force field of the gas atom increases.¹ For organic solvents the observed differences in ΔS^0 over He to A are similar to those for water, but the differences in $\frac{3}{2} R \ln \frac{m_{\text{G}}}{m}$ are much less, in consequence of the relatively large molecular weight of the solvent molecule compared to water. We might conclude that for organic solvents the restriction of the solvent molecules in the field of the solute molecule is relatively important, at any rate in accounting for the variation in ΔS^0 over the range of the inert gases. This point is referred to again in the section on polyatomic gases. For He in C_6H_6 , we might expect these neglected restrictions to be at a minimum, and we will evaluate equation (3) roughly for this case. For a mole of gas per litre solution $\ln \frac{N_{\text{S}} + N_{\text{G}}}{N_{\text{G}}} \sim 2.5$.

The value of V_{G} is uncertain; crude calculations for H_2O^1 , and some considerations of Horiuti for organic solvents⁴ suggest 1.0×10^{-23} c.c., while the average value for a molecule in a pure organic liquid is 0.5×10^{-24} c.c.¹⁰ If the potential curve of the gas molecule in solution

⁹ Guggenheim, Fowler's *Statistical Mechanics*, 1936, 524.

¹⁰ Kincaid and Eyring, *J. Chem. Physics*, 1938, 6, 620.

is parabolic $T \frac{\partial}{\partial T} \ln V_G = 1.5$. Assuming $\bar{V} = 30$ c.c., $\Delta S_G = 10.3$ e.u., and $\Delta S^0 = -0.5$ e.u. ($V_G = 10^{-23}$ c.c.) or -6.5 e.u. ($V_G = 0.5 \times 10^{-24}$ c.c.). The observed value is $\Delta S^0 = -6.6$ e.u.

In view of the large number of uncertainties no definite conclusions may be drawn, but a tentative attempt to co-ordinate the cases of water and organic solvents might be made as follows. It is apparent from the above calculation that the smaller free volume gives a better agreement with experiment. It has already been pointed out that for He, say, in both organic solvents and water similar values of ΔS_A are observed. Now, our previous treatment for water was characterised by the use of a restricted concentration term (less than $(N_S + N_G)/N_G$), and a large value for V_G of about 10^{-23} c.c. The first consideration is almost certainly correct, but the numerical value can only be guessed; similarly, the large value for V_G cannot be taken as definitely established, although it is understandable if our picture is a correct one, namely that the gas molecules in water do not share quasi-lattice points with the water molecules but rather sit in some form of special cavity, which is relatively easily formed at room temperature. For organic solvents, however, if the gas molecules share the quasi-lattice points of the solvent molecules, then we might reasonably expect both the higher concentration term $(N_S + N_G)/N_G$, and the smaller free volume already established for the pure solvent. Then a value of ΔS_A not many units different from that observed for the same gas in water is to be expected.

4. The Solution of Polyatomic Gas Molecules.

(a) The Energy of Solution.

Horiuti⁴ presents data on the heat of solution at constant volume q_V of H_2 , N_2 , O_2 , CO , CH_4 , N_2O , C_2H_2 , C_2H_4 , and C_2H_6 in six organic solvents. $q_V = -\Delta E^0 + T(\alpha/\beta)\bar{V}$, where $\Delta E^0 = RT^2 \frac{\partial}{\partial T} \ln sV_L$, V_L

being the molar volume of the solvent. Since $RT^2 \frac{\partial}{\partial T} \ln V_L \sim 0.25$ k.cal., we can neglect it to a first approximation, and then $q_V \sim -\Delta E_A$. In Fig. 2, we compare his values of ΔE_A (i.e. $-q_V$) with ΔE_A values for the same gases in water (data from Butler¹¹), by means of a plot of ΔE_A against the polarisability of the gas molecule. The circles are for water, the crosses for CCl_4 , and the vertical lines give the spread of values over the other organic solvents. Our first conclusion is that for a given gas ΔE_A is similar for water and organic solvents. Such a conclusion has already been drawn for the inert gases; the anomalous heat of solution (exothermic) of the small gas molecules in water at constant pressure is due to the energy of cavity formation, which is smaller than for organic solvents. Further, in any given solvent a change from H_2 (polarisability $= 0.8 \times 10^{-24}$ c.c.) to C_2H_6 ($p = 4.5 \times 10^{-24}$) changes ΔE_A from -1.5 k.cal. to -7.5 k.cal., while for a given gas in H_2O ($p = 1.48 \times 10^{-24}$) and C_6H_5Cl ($p = 12.2 \times 10^{-24}$) ΔE_A does not alter within ± 1 k.cal. (some of the random differences may be due to experimental error).

¹¹ Butler, *Trans. Faraday Soc.*, 1937, **33**, 229.

In earlier calculations¹ of the interaction energy of an inert gas atom and a water molecule, it was found that the polarisation energy arising from the water dipole is negligible. So we conclude that for the solvents considered ΔE_A is mainly determined by the nature of the gas atom and is much the same from solvent to solvent. This latter conclusion may be simply explained. The London forces mainly determine ΔE_A and for a given gas atom these will depend on the factor $p_G p_S$ (p = polarisability). ΔE_A will tend to stay roughly constant, as for a given separation of centres an increase in p_S will mean an increase in

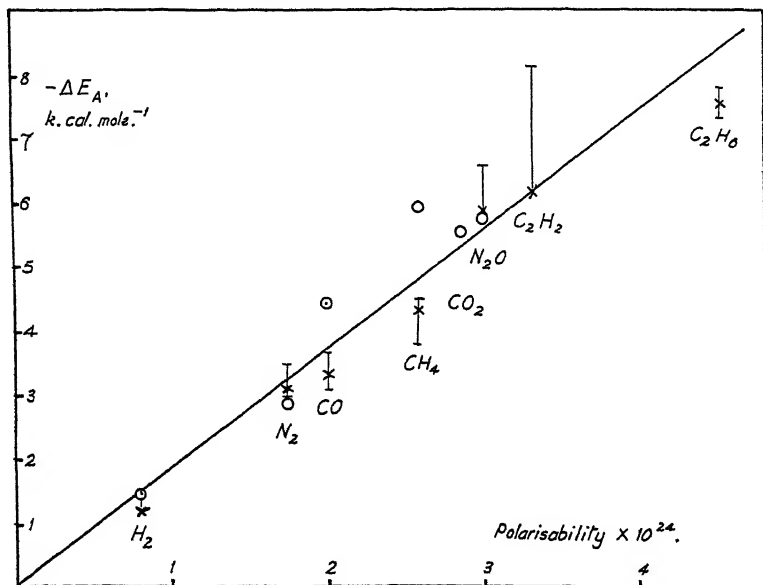


FIG. 2.

ΔE_A per molecule of solvent, but since it is generally accompanied by an increase in the size of the solvent molecule it will also mean a decrease in the number that can be packed around a gas molecule.

(b) The Entropy of Solution.

Bell¹² has calculated the entropies of solution from Horiuti's data, and since a given gas has similar values in the five organic solvents considered, it is sufficient to compare one of them with water. In Table I we compare ΔS^0 for C₆H₆ at 20° C. with Butler's data for water¹¹ at 25° C., due correction for our standard states having been made. We can neglect the temperature difference, since ΔS^0 varies but little with temperature for organic solvents. The partial molal volumes in all cases are known (Table II), and together with data from Table III (ΔS_C for a 10 c.c. "molal cavity" in water at 25° C. = 1.3 e.u.), we can calculate ΔS_C , and hence $\delta\Delta S_C$. Again, we have that $\delta\Delta S_C$ is similar in magnitude to $\delta\Delta S^0$, i.e., a large part of the difference between the entropies of solution of a gas in an organic solvent and in water is to be attributed to the relatively large increase in the entropy of the

¹² Bell, *Trans. Faraday Soc.*, 1937, **33**, 496.

organic solvent associated with the formation of a cavity in it, in which to put the gas molecule.

That the neglected factors, such as the restriction of the solvent in the field of the gas molecule, are important is shown by the factor that variations in the factor $\frac{3}{2} R \ln \frac{m_g}{m}$ will by no means account for the variation in the observed ΔS^0 . These restrictions, in order to give the observed variation in ΔS^0 , must increase rather more rapidly with increase of size of the gas molecule (*i.e.*, their ΔS contribution becoming increasingly negative) than the corresponding increase of ΔS_G . The approximate equality of $\delta\Delta S_G$ and $\delta\Delta S^0$ would indicate that the neglected factors have similar values

TABLE I.

Gas.	ΔS^0 Water (25° C.).	ΔS^0 Benzene (20° C.).	$\delta\Delta S^0$.	$\delta\Delta S_G$.	$-\frac{3}{2} R \ln \frac{m_g}{m}$ Benzene.
H ₂	18.2	7.1	11.1	9.8	0.1
N ₂	22.0	7.7	14.3	13.5	0.9
O ₂	23.5	8.6	14.9	12.2	1.0
CO	22.0	8.4	13.6	13.8	0.9
N ₂ O	23.8	12.2	11.6	11.0	1.3
CH ₄	24.0	9.7	14.3	10.9	0.6

for a given gas in both water and organic solvents. We should expect a polyatomic gas to restrict the neighbouring solvent to much the same extent as the inert gas atom of similar size and polarisability. However, apart from this factor, for water as a solvent we know that frequently polyatomic gases are more restricted in water than the corresponding inert gas (Fig. 3, Part I), and no explanation is at present available for this. It may be that even small polyatomic molecules lose some rotation on solution. We should, of course, expect this for long chain molecules.

Finally, we might mention the difference in the energies and entropies of solution of alcohols in water¹¹ and benzene.¹³ The entropy differences vary from C₂H₅OH, $\delta\Delta S^0 = 18.5$ e.u., to n-C₄H₉OH, $\delta\Delta S^0 = 27.0$ e.u. Assuming for benzene the same partial molal volumes as observed for water,¹⁴ we calculate $\delta\Delta S_G = 11.1$ e.u., and 17.4 e.u. respectively. We should expect larger values of $\delta\Delta S_G$ actually, since the partial molal volumes in benzene will probably be appreciably larger than in water.

5. Variation of ΔE^0 and ΔS^0 with Temperature.

The strong decrease of the observed $-\Delta E^0$ and $-\Delta S^0$ with increase of temperature for the inert gases in water has already been attributed to a strong increase of ΔE_G and ΔS_G with temperature, mainly arising from an increase¹ in α . The polyatomic gases behave similarly in water, as one would expect. The other factor that might vary significantly with temperature is the free volume of the gas molecule in the solvent, V_G . However, for $V_G = cT^{3/2}$ (see p. 1424) we should only expect an alteration in ΔS^0 of 0.9 e.u. over 0 to 100° C., from this source. For organic solvents we should not expect a large variation in ΔE_G or ΔS_G with temperature. In general, over the range 0° C. to 100° C., α increases by only 20 % (Landolt-Bornstein, *Hw. II*, 1227), \bar{V} by 40 %³, and β

¹³ Butler and Harrower, *Trans. Faraday Soc.*, 1937, 33, 171.

¹⁴ Berner, *Z. physikal. Chem.*, A, 1939, 141, 94.

by 100 % (*L.B. Hw. I*, 99), and so $(\alpha/\beta)\bar{V}$ stays roughly constant. So we should not expect ΔE^0 and ΔS^0 to vary much with temperature for the organic solvents, i.e. we should expect a linear $\ln s$ against $1/T$ plot. Such a behaviour is found for the inert gases,⁷ and for N_2O , C_2H_2 , C_2H_4 and ethane³ in organic solvents. A slight curvature is found over a wide range of temperature for some smaller polyatomic gases in organic solvents,⁸ but the effect is much smaller than for the same gas in water. For example, the maximum effect observed by Horiuti is for the case O_2 /Ether, where ΔS^0 alters by 3.5 e.u. over a range of 100° C., to be compared with 14 e.u. for O_2 /water. Most of the variations in ΔS^0 with temperature are much smaller than for the case O_2 /Ether, and may be accounted for by small variations in ΔS_G and V_G ; there is no doubt that the large variations in ΔE^0 and ΔS^0 for solution in water are quite anomalous, as we should expect from this theory.

6. Partial Molal Volumes of Gases.

In Table II we present sufficient data to show that the partial molal volume of a gas \bar{V} is smaller in water than in organic solvents. Van der Waals' b , in c.c. per mole, is larger than \bar{V} for water, but runs roughly

TABLE II.*

Gas.	<i>b</i> , cc. per Mole.	Partial Molal Volume \bar{V} in						
		H ₂ O.	C ₆ H ₆ .	CH ₃ OH.	Ether.	CCl ₄ .	C ₆ H ₅ Cl.	Acetone.
He	23.5	15.5	—	—	—	—	—	—
H ₂	26.6	18.9	36.3	35.2	50.5	37.7	33.8	38.3
N ₂	38.5	32.5	52.7	—	65.7	53.1	49.6	55.1
CO	39.9	28.5	51.8	—	61.9	52.5	46.1	53.1
O ₂	31.8	25.8	46.2	—	56.0	45.3	43.0	47.7
CH ₄	42.8	50.0	52.0	—	59.2	52.4	48.9	54.9
CO ₂	42.7	35.0	47.9	41.2	44.8	48.2	44.7	44.7
N ₂ O	44.1	37.0	47.2	—	—	46.9	44.9	46.1

* Data mainly at 25° C., except CO and O₂ in H₂O (0° C.). The references are: Angström, *Wied. Ann.*, in 1882, 15, 297; 1888, 33, 223. Bellati and Lussana, *Z. physik. Chemie*, 1890, 5, 281. Horiuti,³ Michels, *et. al.*¹⁶

parallel to it. Two reasons for the first difference suggest themselves (a) in water there is already 9 c.c. of empty space per mole, since a close-packed structure of water molecules of radius 1.4 Å occupies only 9 c.c. per mole; (b) the water in the neighbourhood of the solute is modified towards the close-packed structure. The latter suggestion is supported by the fact that solutes like ether lower the temperature of maximum density of water,¹⁵ and lower the compressibility of water in small concentrations despite their own high compressibility.¹⁶ The existence of a modified water structure in the neighbourhood of a solute molecule is supported by the fact that for gases in water \bar{V} first decreases with increase of temperature, passing through a minimum¹⁷ at 50° C. On

¹⁵ See Tamman, *et al.*, *Z. anorg. Chem.*, 1928, 174, 231; 1930, 194, 273; Landolt-Bornstein, *Erg. IIa*, 279, IIIa, 404.

¹⁶ Ritzel, *Z. physikal. Chem.*, 1907, 60, 319; Richards and Chadwell, *J. Amer. Chem. Soc.*, 1925, 47, 2283.

¹⁷ Michels, Gerver and Bijl, *Physica*, 1936, 3, 797.

the other hand, where we insert the solute into a simple close-packed liquid, we might expect an increase in \bar{V} with T analogous to the increase of molal volume V_L of the solvent with T . This is found for organic solvents, where the average value of $\frac{\partial}{\partial T} \ln \bar{V}$ is about 3×10^{-3} (calculated from Horiuti's data³), while an average value of $\frac{\partial}{\partial T} \ln V_L$ is 1×10^{-3} . In connection with the small differences between \bar{V} for a gas in a series of organic solvents, since an organic solvent is not a continuous medium we might expect the size of the solvent molecules to have an effect.

7. The Energy of Cavity Formation in a Solvent.

A comparison of the three available methods of estimating ΔE_C is enlightening. In view of uncertainties in α , β and molecular radius values the calculations cannot be regarded as exact. Let us make 1 mole of cavities, *i.e.* N cavities, each of volume v c.c. We will calculate ΔE_C for $Nv = 10$ c.c., *i.e.* $v = 1.65 \times 10^{-23}$ c.c., cavity radius $r = 1.58\text{\AA}$, and surface area of cavity $4\pi r^2 = 31.4 \times 10^{-16}$ cm.².

(a) If we assume $Nv = \bar{V}$, the expansion of the solvent consequent upon formation of the cavities (*i.e.* the partial molal volume of the gas), the method of Part I gives

$$\Delta E_C = T(\alpha/\beta)\bar{V} = T(\alpha/\beta)Nv = 70.5(\alpha/\beta) \text{ cal. mole}^{-1}.$$

The values in Table III are for 20° C. (α , *L.B. Hw. II*, 1224, 1232; β , *L.B. Hw. I*, 94).

(b) If we assume a similar structure for the internal spherical surfaces as for the macroscopic solvent surface, then we can calculate ΔE_C from γ , the surface free energy in ergs./cm.². For our case

$$\Delta E_C \sim \Delta H_C = 45.4 \left(\gamma - T \frac{\lambda \gamma}{\delta T} \right) \text{ cal. mole}^{-1}.$$

The data are mainly from Jaeger, *Z. anorg. Chem.*, 1917, 101, 1, and *L.B. Erg. IIa*, 148. The results are in column (b), Table III.

(c) Lange and Martin¹⁸ suggest $\Delta E_C = \Delta E_{\text{vap}} \left(\frac{r}{r_s} \right)^2$ for formation of a mole of cavities of radius r in a solvent of molecular radius r_s .

$$\Delta E_{\text{vap}} = L - RT,$$

where L is the latent heat of vaporisation of the solvent (*L.B., Hw. II*, 1434, 1585, *Erg. IIIc*, 2730). The value of r_s used is the mean of viscosity and evaporation heat data (*L.B., Erg. IIIa*, 105), and the values of ΔE_C are sufficiently accurate despite the uncertainty in r_s , to justify the following discussion (*i.e.* assuming the r^2 relationship is significant, as it probably is to a crude approximation).

The internal latent heat of evaporation, ΔE_{vap} is considered by Eyring¹⁹ to give the energy required to form a mole of cavities, the same size as the molecules, in a liquid. These cavities will be on quasi-lattice points, and we may regard method (c) as roughly giving the

¹⁸ Lange and Martin, *Z. physikal. Chem.*, 1937, 180, 238.

¹⁹ Eyring, *J. Chem. Physics*, 1936, 4, 283.

energy required to put a solute molecule onto a quasi-lattice point of the solvent. We might expect a similar result from method (b), and in fact for organic liquids the two methods give similar values. Moreover, for organic solvents method (a) gives comparable results with (b) and (c), and a more exact agreement would be obtained if the partial molal volume \bar{V} corresponding to Nv were used, since there is evidence that for all solvents \bar{V} is two to three times Nv . So, for organic solvents, all three methods may be used to estimate ΔE_G , and hence ΔE_A from the observed value of ΔE^0 . In these cases we may regard the gas molecules

TABLE III.

Solvent.	$f_s \cdot A$	ΔE_G K. cal. mole ⁻¹ , at 20°C.		
		By method a.	By method b.	By method c.
Water . . .	1.4	0.32	5.31	13.1
EtOH . . .	2.0	0.86	2.01	6.0
Hexane . . .	3.2	—	2.25	1.69
CHCl ₃ . . .	2.6	0.94	3.00	2.73
Acetone . . .	2.4	1.05	2.67	3.08
Ether . . .	2.7	0.62	1.92	1.96
CCl ₄ . . .	3.0	0.94	2.92	2.05
Me Acetate . . .	2.4	1.04	—	2.87
C ₆ H ₆ . . .	2.5	1.01	3.4	3.01

as sharing the quasi-lattice points of the solvent, and for close-packed liquids with a minimum of structure it is difficult to see what else can occur. For water, with its open four co-ordinated structure and directed bonds, we might expect the possibility of special kinds of cavity formation. We may say that the discrepancy between methods (b) and (c) for water indicates roughly that only one H₂O—H₂O bond (value 5 k.cal.) is broken in forming a mole of macroscopic surface (to form a hole the size of a water molecule on a quasi-lattice point involves breaking 2 bonds, total value 10 k.cal.). The wide discrepancy between methods (a) and (c) for water indicates that an even greater compensation of bonds occurs when a cavity is made in water at room temperature. We shall discuss this in the next section. The simplest point of view is that the solution of gas molecules (the case for which estimation of ΔE_G by (a) is significant) occurs into spaces between the quasi-lattice points of water. These spaces are easily enlarged by the conversion of water in the neighbourhood towards the close-packed structures, *i.e.* in the direction Water I \rightarrow Water III. At high temperatures, however, where water is tending to be close-packed, this compensation becomes impossible, and then solution must occur onto quasi-lattice points. Here (250° C.) methods (a) and (c) yield more comparable values in consequence of the increase of α/β and decrease of L with temperature increase. Actually, water reaches a fairly stable structure around 50° C. long before it is close-packed, and starts to behave in a similar way to the solution of gas as organic liquids, with a similar value of ΔE_G (method (a)). Even at room temperature, however, certain solutes with strong force-fields, *e.g.* D₂O, or ions, might be expected to displace H₂O molecules from quasi-lattice points, in which case method (c) is appropriate for estimating ΔE_G .

8. The Isothermal Expansion of Liquids.

The detailed discussion of Table III is best made under this heading. The function $(\partial E/\partial V)_T = \alpha/\beta$, frequently referred to as the internal

pressure, gives the increase in internal energy with volume at constant temperature. In the first instance, we might interpret the fact that $(\partial E/\partial V)_T$ is positive for organic liquids by the theory that the expansion occurs by the uniform separation of all the molecular centres, the forces between which are attractive at all ordinary pressures. Recently the existence of holes in a liquid has been shown to account successfully for a number of properties,¹⁹ and this view may be used for our problem. Then a comparison of columns (a) and (c) would suggest that the isothermal expansion of organic liquids occurs by the formation of holes on quasi-lattice points. As previously pointed out, methods (a) and (c) would give similar values if a "fused-cavity volume" of 10 c.c. corresponds to a total increase of liquid volume of 20-30 c.c. Such a correspondence might be expected because of (i) a modification in solvent volume occurs around an empty quasi-lattice point, (ii) while a mole of "fused-cavities" of radius r occupy only $\frac{4}{3}\pi r^3 N$, a mole of close-packed molecules of radius r occupy a larger volume, $5.66 N r^3$ (departures from perfect close-packing, which are to be expected, will increase this discrepancy). An explanation of the more complicated case of water may be based on the structure suggested by Bernal and Fowler.²⁰ The negative value of $(\partial E/\partial V)_T$ observed below 4° C. arises from the change from quartz water (II) to the lower energy tridymite water (I) with increase of volume. Above 4° C. $(\partial E/\partial V)_T$ is positive but much smaller than for organic liquids. In this case, isothermal expansion can be regarded as occurring through the formation of holes in quartz water II, together with a modification towards the close-packed water III, the energy of formation of which helps to lower $(\partial E/\partial V)_T$. In organic liquids no compensating changes of structure are possible, and higher values of $(\partial E/\partial V)_T$ are observed, in spite of the fact that their intermolecular forces are frequently weaker than those of water. We may point out that a significant modification of the water structure occurs around 50° C. (see, e.g. Magat²¹), which we might tentatively call a modified quartz structure, II'. Over 0° C. to 50° C. a continual breakdown $I \rightarrow II \rightarrow II'$ occurs, but above 50° C. water behaves in most ways like organic liquids, the structure II' being fairly stable, and only becoming close-packed at much higher temperatures. It is probable that it is this structure II', rather than III, which is formed around a cavity or solute molecule, and such a suggestion might be tested by Raman spectra.

Tammann²² identified the 0-50° C. changes in water as associated with the breakdown of water I, but his estimate of the concentration of water I at 0° C. as 15 % is much higher than that of Bernal and Fowler, who consider it to have practically vanished at 4° C. Tammann's considerations would, however, fit in with the more complicated breakdown of structures suggested here. Tammann²³ interpreted the minimum of gas solubility around 50° C. on the theory that the gas had a much stronger interaction with water I than the other water species. We should rather say that solution occurs onto those points in a hypothetical "static water structure," where modifications of structure in the direction $I \rightarrow II \rightarrow II' \rightarrow III$ can occur.

²⁰ Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.

²¹ Magat, *Trans. Faraday Soc.*, 1937, **33**, 119.

²² Tammann, *Z. anorg. Chem.*, 1926, **158**, 1.

²³ Tammann, *ibid.*, 17.

Summary.

1. While the energy of solution of a gas molecule is much the same in a series of organic solvents, it is appreciably more negative in water. It is suggested that the main part of this difference resides in the different energies required to form a cavity in the solvent in which the gas molecule is placed. A similar difference exists between the entropies of solution which arises from a difference in the entropies of cavity formation.

2. A further discussion of the entropies and energies of solution is made, and a tentative co-ordination of the known facts of solution is attempted. The problem of solubility bears on that of the isothermal expansion of liquids. In both cases it is suggested that for organic solvents holes are made on the quasi-lattice points of the solvent. For water at room temperature structural modifications are possible which complicate the problem of cavity formation.

3. Attention has been drawn to certain factors which could be neglected in a first account of the inert gases in water, but which would appear to be important for an account of the entropies of solution of a series of gases in an organic solvent.

The author's best thanks are due to Professor E. K. Rideal, F.R.S., for his interest in this work. He expresses his indebtedness to the Department of Scientific and Industrial Research for a Senior Award.

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EXPERIMENTS WITH ATOMIC HYDROGEN: A SEARCH FOR HIGHER HYDRIDES OF NITROGEN, PHOSPHORUS AND SULPHUR.

By K. G. DENBIGH.

Received 18th September, 1939.

Elements in Groups VB, VIB and VIIB of the Periodic Table show a lower valency towards hydrogen than towards the halogens. Phosphorus and sulphur, for example, form the fluorides PF_5 and SF_6 whilst the highest known hydrides are PH_3 and H_2S . As no explanation of this behaviour seems to have been given, it was decided to attempt the preparation of the hypothetical hydrides PH_5 and SH_6 . For this purpose, PH_3 and H_2S were brought into contact with atomic hydrogen.

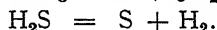
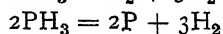
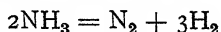
The first short period forms an exception to the above remarks. From Group IV to Group VII the valency, towards both hydrogen and the halogens, follows the sequence 4, 3, 2, 1, and the reason for this, of course, is that the number of electrons in the corresponding electron group is limited to eight. A hydride of nitrogen, for example, higher than NH_3 would not be expected and the existence of NH_4 in the so-called ammonium amalgam is unlikely. It seemed worth while, however, to investigate the reaction of atomic hydrogen with NH_3 .

The behaviour of both NH_3 and H_2S with atomic hydrogen has been described by Boehm and Bonhoeffer.¹ NH_3 was unchanged,

¹ Boehm and Bonhoeffer, *Z. physik. Chem.*, 1926, 119, 385.

whilst H_2S caused the hydrogen atoms to re-combine with separation of sulphur. The experimental method, however, was not one which would have allowed these authors to have detected small amounts of higher hydrides.

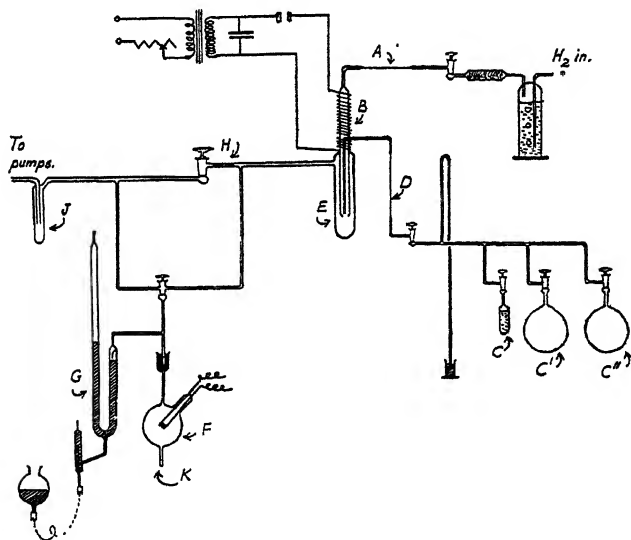
In the present work the reaction products were condensed in liquid air and were then analysed. This was carried out by thermal decomposition at constant volume. If the reactant gases had remained unchanged, the analyses would have been according to the equations:—



The measured pressure increases would then have been 100 %, 50 %, and nil respectively. If any higher hydrides had been formed, greater pressure increases would have been observed.

Experimental.

Moist hydrogen was drawn through the capillary A, of the diagram, at 20-30 c.c./min. and its pressure was maintained at about 0.3 mm. by



means of a mercury vapour pump and a Hyvac. It was dissociated at B by means of an electrodeless discharge. The other reactant gases were withdrawn from the storage vessels C, C', and C'' and were passed through a second capillary D to meet the atomic hydrogen at a nozzle in the vessel E, cooled in liquid air. The flow rate of these gases was about a tenth of the hydrogen rate. Samples of the condensed products were subsequently volatilised into the bulb F, connected to a constant volume manometer G. Decomposition was effected by means of a heated platinum filament, or, in the case of the phosphine experiment, by heating the bulb itself. It was continued to a steady pressure, as observed on a cathetometer. Constant temperature was attained by means of a water bath.

A platinum spiral was inserted in the pumping tube at H to prevent atomic hydrogen reaching the tap grease. Normally it glowed brightly but occasionally it became inactive. That this inactivity was not due

to the absence of hydrogen atoms was proved by inserting a fresh piece of platinum. Poisoning in the catalysis of hydrogen atom recombination does not seem to have been reported previously.

The glowing platinum was not completely effective in removing hydrogen atoms, for a blue-green luminescence was sometimes observed in the mercury vapour pump and was probably the chemiluminescence attributed² to the formation of HgH . It even appeared with the trap J immersed in liquid air.

As a check on their purity, samples of the NH_3 , PH_3 and H_2S were analysed by thermal decomposition. In all cases, the observed pressure changes were within 0.4 % of theoretical. In another check on the experimental method, an examination was made of the reaction product which was condensed when moist hydrogen alone was passed through the apparatus, with the discharge taking place. Its vapour pressure was that of water and it gave no volume change when its vapour was examined in the decomposition bulb. It was satisfactory that no SiH_4 was formed.

In experiments *without* liquid air under the reaction vessel, NH_3 , PH_3 and H_2S were all found to cause the recombination of hydrogen atoms, as shown by the quenching of the glow at the platinum spiral. H_2S also gave a deposit of sulphur and PH_3 gave a brilliant yellow mirror on the glass. This was not yellow phosphorus but was probably the substance known as the solid lower hydride. Both deposits disappeared under the influence of the atomic hydrogen alone.

With the reaction vessel immersed in liquid air, the condensed products were all white, except in the case of phosphine where the material was yellowish, probably again due to the presence of lower hydrides. The products were analysed in a number of fractions according to volatility. In order to correct the observed pressure changes for the presence of water vapour, especially in the least volatile fractions, this vapour was condensed out in the tube K by means of liquid air after decomposition was complete. Non-condensable gas was then pumped out of the bulb and the partial pressure of water vapour was measured on the manometer.

The measured pressure changes were all within 0.5 % of theoretical, indicating no detectable formation of higher hydrides. The following results on H_2S are typical:—

	Most Volatile Fraction.	Middle Fraction.	Least Volatile Fraction.
Pressure before decomposition .	35.8 ₃ mm.	32.6 ₁ mm.	76.0 ₈ mm.
Pressure after decomposition .	35.6 ₈ mm.	32.5 ₈ mm.	76.0 ₈ mm.

In the case of the product obtained with PH_3 , only the most volatile part was examined, for the presence of lower hydrides in the remainder would have interfered with the detection of PH_3 . If the latter had been formed, it would, however, have been expected to be present in the most volatile fraction and this was found not to be the case.

The analyses were, of course, carried out at room temperature and it might have been possible for a higher hydride to have existed at liquid air temperature but decomposing into the normal hydride and hydrogen during the warming up. It was found, however, that the various reaction products, after volatilisation, could again be recondensed completely, *i.e.* no appreciable quantity of hydrogen had been formed. This test was not carried out in the case of the hydrogen sulphide experiment.

² Bonhoeffer, *Z. physik. Chem.*, 1925, 116, 391.

Concluding Remarks.

The non-existence of hydrides of elements in Groups VB, VIB and VIIB corresponding to the highest halides is surprising, for these elements might be expected to form as many bonds with hydrogen atoms as with halogens. Pauling³ considers that in a fluoride such as PF_5 , the completely covalent structure, with a decet of shared electrons, is probably of minor importance since it would involve the unstable $3d$ orbitals. Instead, it is believed that this molecule has an ionic structure in which a negative fluorine ion resonates amongst the five positions and the phosphorus atom has a normal octet and a positive charge.

If this view be correct, it may account for the non-existence of PH_5 , since in this the hydrogen atoms would be *more* electropositive than the phosphorus atom and an ionic structure of the above type is therefore unlikely.

Another possibility is that the highest known hydrides may show a lack of tendency to add on extra hydrogen for the same reason as that which accounts for the inertness of the rare gases. Thus PH_3 , H_2S and HCl all possess exactly the same total number of electrons as argon: AsH_3 , SeH_2 and HBr possess the same number as krypton and so on. The extranuclear structure of these hydrides may therefore bear some resemblance to those of the rare gases. In the hydrides, of course, protons are embedded in the electron cloud and are bound to modify the structure in spite of the equal number of electrons. But the case is very different with the corresponding lower fluorides, PF_3 , etc., for here the *total* number of electrons is not the same as in a rare gas and the fluorine nuclei have a much higher charge than the protons of the hydrides.

Some support for this view is given by the steady and systematic falling off in the valency towards hydrogen in the sequence 4, 3, 2, 1 for elements in Groups IV to VII.

Summary.

Ammonia, phosphine and hydrogen sulphide were brought into contact with atomic hydrogen in an attempt to prepare higher hydrides. All three gases caused hydrogen atoms to recombine and the two latter were also decomposed. The reaction products were analysed but there was no evidence of higher hydride formation.

Possible reasons for the non-existence of hydrides corresponding to PF_5 and SF_6 have been briefly considered.

A case of poisoning of platinum in the catalysis of hydrogen atom recombination is also reported.

The author wishes to express his thanks to Prof. N. K. Adam, F.R.S., for his interest in this work, and to the students, Messrs. Godfrey, May and Slade, for experimental help.

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³ Pauling, *The Nature of the Chemical Bond*, 1939, p. 90.

ELECTRICAL CONDUCTION OF COMMERCIAL BORON CRYSTALS.

BY J. H. BRUCE AND A. HICKLING.

Received 21st September, 1939.

1.

Although it has long been known¹ that the passage of electricity through boron shows a gas-discharge characteristic, an increase in the current above a certain value being accompanied by a fall in the potential across the specimen, references in the published literature are scarce and no detailed account of the phenomenon appears to be available. Thus Weintraub² has given a general description of the effects found on large slabs of the fused material, which he describes as amorphous, with particular reference to technical applications both of the "trip-voltage" effect and of the very high negative temperature coefficient, and Lyle,³ in examining fused rods, showed that the known data concerning the former effect could in fact be deduced from the latter; in particular, the incidence of a time lag, sometimes of several minutes, in the electrical break-down, similar to that found with ordinary insulators. Nevertheless such investigations refer to the average behaviour of large samples, and moreover to their behaviour either in stationary states or over long periods of time, and are inadequate for a sufficient understanding of the phenomenon.

It is hoped, therefore, that the following notes will be of interest, although the comprehensive investigation which had been planned has been prevented by the present emergency.

2.

Observations were made on single crystals of commercial boron, supplied by the British Drug Houses Ltd., both with direct and alternating current,

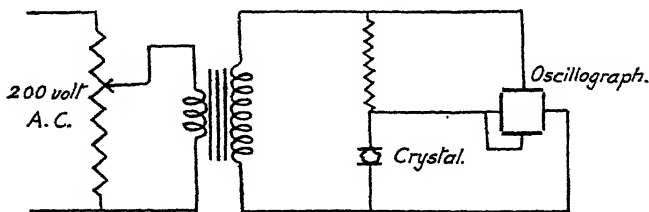


FIG. 1.

under conditions which permitted the instantaneous values of current and potential to be studied. Small crystals, invariably less than 1 mm. cube and usually much smaller, were pressed between well-tinned metal electrodes. In the case of D.C. observations, a heavy series resistance was introduced to prevent excessive currents, and measurements were made in

¹ Mellor, *Comprehensive Treatise*, Vol. V, p. 13.

² *Trans. Amer. Electrochem. Soc.*, 1909, 16, 165; *J. Ind. Eng. Chem.*, 1911, 3, 299.

³ *Physical Review*, 1918, 11, 252.

the usual manner. For A.C., leads were taken from the electrodes and from a series resistance to the plates of a cathode ray oscillograph, the current being thus recorded as a function of the applied potential (Fig. 1).

Typical direct current observations are shown in Fig. 2, the series resistance being *ca.* 10,000 Ω . It may be noted that the relatively enormous currents (sufficient to produce a red heat) which the small crystal had carried, did not prevent the path from being approximately reversible, and when care was taken to limit the overheating, greater consistency was observed; this is discussed more fully below. The starting potential, at which the crystal ceased to act as a high resistance, and maintenance potential approached for heavy currents, varied greatly from one sample to another, depending on the crystal size and probably on the previous thermal history, though no exact relation could be found. Effects of orientation were not investigated, nor was it determined whether the entire crystal or only certain regions are active. While the behaviour of nearly all the crystals eventually conformed to the type shown, it was found that a substantially higher potential, ranging from 200 v. upwards, was usually necessary to produce initial break-down. There was no close correlation between this and the true reproducible starting potential, although for larger crystals, especially if the current was strictly limited, the difference between them appeared to be reduced. It is uncertain whether this effect was a property of the crystal itself or was connected with the breaking down of surface films; it is of interest that the burning-in process often showed a considerable time lag, and on a few samples was not successfully accomplished, and it is possible that this was in fact the effect studied by Lyle.³

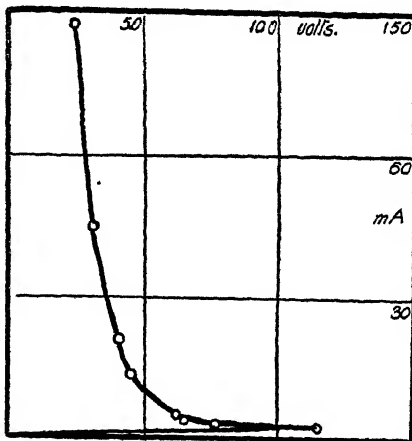


FIG. 2.

The observations with alternating current, being recorded photographically, were confined to cyclically reproducible phenomena, and hence only crystals which had been fully burnt-in for the relevant range of currents could be studied. Oscillograms for a particular sample at progressively increasing applied voltages are shown in Fig. 3, A, B, and C. At first the crystal behaves throughout as a high resistance; when a certain voltage is reached, a momentary surge of current passes at the peak, and subsequent voltage applied to the circuit does not produce any further rise across the crystal, but, on the contrary, the surge of current is accompanied by an actual decrease of voltage, as is shown more clearly in Fig. 3 D, taken under precisely the same conditions as C but with a more extended voltage scale. In the series shown, the starting voltage was approximately 55 v. and the maximum current passed about 10 m.amp. The observations on fully burnt-in crystals were usually recognisably of the type shown, although the sharpness of incidence of the current surge and negative resistance phase varied greatly from specimen to specimen, Fig. 3 E being an extreme example, and for a given specimen depended on the constants of the external circuit. If a very large current was passed, however, the characteristics became blurred, and eventually the sharp cut-off disappeared; this is probably a thermal effect. Very occasionally a much more complicated characteristic was observed, still showing sharp cut-off

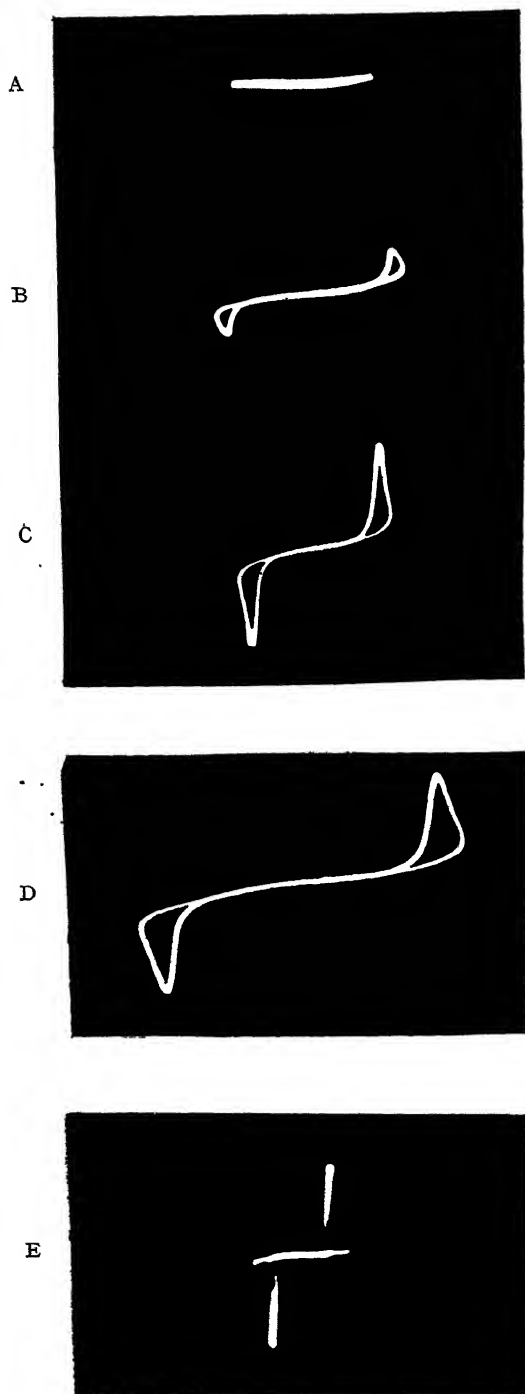


FIG. 3.

points, but retaining a low instantaneous value of the resistance at the zero of the applied voltage. It was impossible to establish the conditions for the incidence of this type of discharge.

3.

It is clear that, at these frequencies, except under extreme conditions, the usual behaviour of the discharge is essentially such as might be expected from the static characteristic observed with direct current (Fig. 1), including the occurrence, during each half-cycle, of a phase of "negative resistance," immediately following a period of approximately linear increase of current with potential, and corresponding to a constant high ohmic resistance; moreover a very high degree of reproducibility in the characteristics of the crystal is indicated.

The passage from ohmic resistance to fully developed gas-discharge type certainly occurs repetitively in a period of lower order than one millisecond, and does not vary continuously about a mean value, except under conditions in which local heating may be expected to develop.

These observations, therefore, indi-

cate that whatever be the fundamental mechanism of the change, the gas-discharge characteristic is not of thermal origin, and that this theory leads to an over-simplified and incorrect view of the process.

Summary.

Observations with direct and alternating currents on the conduction of electricity in boron crystals are described. It is shown that, after a preliminary burning-in process, the state of negative resistance is fully developed in a very short period, and that the results for any given crystal show a high degree of self consistency, and it is suggested that the existing theory of the process is inadequate for their description.

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LIMITING DENSITIES AND MOLECULAR WEIGHTS OF OXYGEN; CARBON DIOXIDE, SULPHUR DIOXIDE AND HYDROGEN SULPHIDE.—ATOMIC WEIGHTS FOR CARBON AND SULPHUR.

By E. MOLES, (MISS) T. TORAL AND A. ESCRIBANO.

Received 3rd October, 1939.

If the weights of equal volumes of a gas and of oxygen at 0° and under different pressures between 0 and 1 atmosphere are determined and the obtained values referred to the normal value of p and are put into two series:—

$$\begin{array}{ccccccc} L_p, & L'_p, & L''_p & . & . & . & L_{lim} \\ L^0_p, & L^0'_p, & L^0''_p & . & . & . & L^0_{lim} \end{array}$$

we can, by linear extrapolation to zero pressure, obtain the limiting densities and therefore the density of the gas under ideal (Avogadro's) conditions.

Since the gas laws are only exact at indefinitely low pressures, the application of Avogadro's principle that the molecular weights of gases are proportional to their densities, *i.e.*,

$$\frac{M}{d}, \frac{M'}{d'}, \frac{M''}{d''}, \dots \text{const.}$$

is only strictly true when the limiting densities L_{lim} , L'_{lim} , L''_{lim} are employed in the calculation. Hence, if we take in the above system of proportional numbers $M = 32,000$ (conventional molecular weight for oxygen), $M' = 32,000 L'_{lim}/L_{lim}$ is the most simple and logical expression for Berthelot's rule of the limiting densities.¹ We can take also the relative values of density as density ratios r , r' , $r'' \dots$, from which the limiting ratio r_0 for $p = 0$ can be extrapolated. Consequently $M' = 32,000 \times r_0$.

The best method of extrapolating experimental results in order to obtain the limiting densities is still under discussion. From van der

¹ *C.R. Acad. Sci.*, 1898, 126, 954.

Waals' equation and other theoretical considerations, the relationship between compressibility and, therefore, between normal density and pressure should be represented as a function of the second degree $L_p = a + bp - cp^2$. For the less compressible gases the p^2 term can be neglected.

It has recently been shown² that for all gases, including the exceedingly compressible ones, the relationship between L_p and p is certainly strictly linear over the pressure range between 0 and 1 atmosphere for which Berthelot's rule applies and within the limit of error (10^{-5}) of our experiments. No difference is noticed between less and more compressible gases when values are used which have been corrected for adsorption.

It has been shown³ that the determination of molecular and atomic weights within an accuracy of 10^{-4} requires a knowledge of density values and therefore of all related data (pressure, temperature; weight of gas) to at least 10^{-5} . This degree of accuracy may be easily obtained by following the improved technique which has been fully described elsewhere.^{3,4} In previous work we recommended, on account of practical limitations, that measurements should be taken over the range between 0.5 and 1 atmosphere. In this paper a full account is given of recent experiments with compressible gases over the range between 0.25 and 1.0 atmosphere, in which the precision has been kept within 10^{-5} . This enables extrapolation to the limiting densities to be made with greater accuracy.

Apparatus.

Density was measured with the volumeter by the displacement as well as by the condensation method. Two different volumeters A and B were used, both of which comprised two independent flasks of about 2400 ml., each of which could be filled either together or separately, with a known weight of gas, thus giving two different values of density. Volumeter A had previously served for determining the density of ammonia. It was made entirely of Thuringian glass and served in the present research for density measurements on oxygen (I), ethylene and sulphur dioxide. The final apparatus is shown diagrammatically in Fig. 1. Volumeter B, of the same size, was used for measuring the limiting densities of oxygen (II), carbon dioxide and sulphur dioxide (II). It was used originally to measure the correction for adsorption. The measuring system (bulbs V, V', barometer B, weighing apparatus C and connecting tubes) was made wholly of Jena glass which adsorbs three or four times less than Thuringian glass.⁵ The whole measuring system together with the mercury reservoir R was kept at 0° C. in ice to avoid any correction for temperature. Raising or lowering the mercury in the barometer was effected by letting in or removing dry pure air through tap t . Thus mercury never came in contact with greased taps or rubber tubing. The setting of the mercury to the fixed pointer p in the shorter line of the barometer was always made with a rising meniscus. This meniscus always remained very clean.

² E. Moles and T. Toral, *Monatsh.*, 1936, **69**, 342; *Anal. Fis. Quim.*, 1937, **35**, 42; E. Moles, *J. Chim. physique*, 1937, **34**, 19; *Anal. Fis. Quim.*, 1937, **35**, 134; E. Moles and T. Toral, *Z. anorg. allg. Chem.*, 1938, **236**, 225; E. Moles, *Arch. Sci. phys. nat.* (5) 1938, **20**, 59; E. Moles, *Les déterminations physico-chimiques des poids moléculaires et atomiques des gaz* (Inst. int. Cooperat. int., 1938, Paris); E. Moles, *Bull. Soc. chim. Belgique*, 1938, **47**, 405.

³ E. Moles and T. Toral, *Z. anorg. allg. Chem.*, 1938, **236**, 225.

⁴ E. Moles and T. Toral, *Monatsh.*, 1936, **69**, 342.

⁵ M. Crespi and V. Alexandre, *Anal. Fis. Quim.*, 1934, **32**, 931; 1936, **34**, 315.

We give the following characteristics of the volumeter :

Volumeter A.	v = Volume.	w = Weight.	Contraction per 1 atm.
Bulb I. . .	2559.56 ml.	219.2 g.	— 0.465 ml.
„ II. . .	2381.09 „	246.1 „	— 0.360 „
Volumeter B.			
Bulb. J ₁ . .	2273.14 „	350.0 „	— 0.230 „
„ J ₂ . .	2270.86 „	322.5 „	— 0.240 „

to which the volume of the connecting tubes and of the dead space in the shorter line of the barometer must be added to obtain the total volume. The contraction of the bulb between the different pressures was calculated

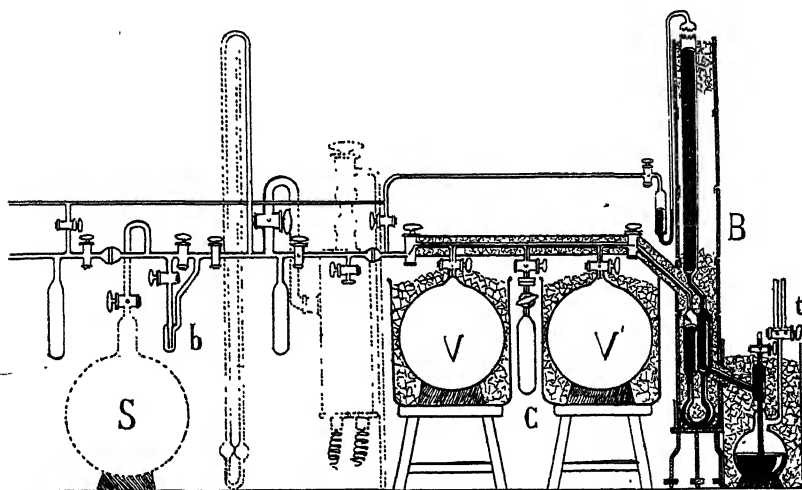


FIG 1.

after the formula of Moles and Miravalles,⁶ viz., $c = v/w \times 15.5 \times 10^{-5}$ ml. The following figures show an example of the changes of this correction :—

Pressure	1.00000	0.750000	0.66667	0.50000	0.33333	0.250000 atm.
Bulb I.	2559.56	2559.45	2559.40	2559.33	2559.25	2559.20 ml.

Changes due to breakage and subsequent repair of the apparatus proved to be negligible.

Pressures.

Observations were made with a reading microscope to ± 0.01 mm. on glass scales mounted in front of the barometer. Scale A requires a correction of length of $+199 \times 10^{-6}$ mm. per mm. and has the expansion coefficient $\beta 9.3 \times 10^{-6}$, scale B requires correction of $+381 \times 10^{-7}$ mm. per mm. and $\beta = 9.2 \times 10^{-6}$ as measured in the precision comparator. To refer the measured pressures to 45° latitude and sea level, we used the factor 0.999323 experimentally determined in our Institute. As has been said, readings were always made *per ascensum*, which gives a very clean meniscus and in every case the heights of the upper and of lower

⁶ J. Chim. physique, 1924, 21, 1.

meniscus were the same within ± 0.001 mm., so that no correction is required. For example:—

Pressure	.	1.0000	0.75000	0.6250	0.50000 atm.
Upper meniscus	.	0.901	0.904	0.903	0.907 mm.
Lower	„	0.902	0.904	0.902	0.905 „

Temperature.

The limiting densities method requires that both the examined gas and oxygen be kept at the same temperature near 0° C. It is very important to ensure the constancy of this temperature, rather than its exact value. We find that constancy within $\pm 0.001^\circ$ is easily obtained by using common ice washed with distilled water. We give a series of readings on the Beckmann thermometer as an example: 5.229° , 5.227° , 5.227° , 5.229° , 5.228° , 5.228° , mean 5.228° . Using pure ice manufactured by us with distilled water 5.228° was read.

Weighing of the Gases.

Gases were weighed by double weighing and employing a counterpoise on a precision balance with the sensibility ± 0.01 mg. with a load of 200 g. By the displacement method (e.g., for oxygen) the weight of evolved gas

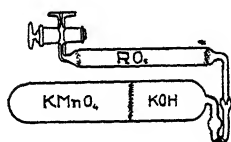


FIG. 2.

is determined by difference in the weight of the gas generator before and after heating. A model of the gas generator is given in Fig. 2. In the condensation method (CO_2 , C_2H_4 , SO_2) the gas was always condensed in weighing tubes (see Fig. 1) charged with about 20 g. activated charcoal which had been previously dried and purified by heating it to 200° *in vacuo*, washing out several times with pure gas and pumping off. The gas condenser was cooled in liquid air. Desorption took place very easily and desorbed gas was recondensed many times and used again and, since it always showed identical density, was very pure.

Preparation of Gases.

The individual gases were prepared as follows:—

Oxygen.—Purest recrystallised KMnO_4 charged in a gas generator was heated to 250° *in vacuo*. The evolved gas was passed over solid KOH through a drop of mercury and dried over P_2O_5 , all contained in the gas generator (Fig. 2). The purity of the oxygen was ascertained by comparing the density of the different samples.

Ethylene was prepared by the dehydration of pure ethyl alcohol over activated Al_2O_3 (obtained by heating $\text{Al}(\text{NO}_3)_3$ to 350° – 400°) heated to 350° C. The evolved gas was passed through a condenser immersed in Thilorier mixture (solid CO_2 + acetone), washed in acidified solution of FeSO_4 and dried over conc. H_2SO_4 and P_2O_5 .

Another sample of ethylene was prepared by heating on a sand bath to 200° – 220° a mixture of 75 p. of metaphosphoric acid (after Moissan) with 25 p. alcohol to which was added with some P_2O_5 and sand. It was purified by cooling to -80° in Thilorier mixture, washed through 50 per cent. KOH solution and then dried, liquefied and fractionated.

Carbon dioxide.—One sample of this gas was prepared by heating to 95° – 100° C. in a vacuum purest recrystallised Na_2CO_3 dried previously at 70° C. The evolved gas was cooled in a mixture of common salt and ice, dried over H_2SO_4 and P_2O_5 and then condensed and sublimed.

Another sample was obtained by heating to 360° – 380° C. pure dried MgCO_3 and then purifying it in a similar manner.

Sulphur dioxide.—Compressed SO_2 gas from a cylinder was dried over conc. H_2SO_4 and P_2O_5 , then condensed and fractionated.

Another sample was prepared by the action of hot concentrated H_2SO_4 on mercury in a high vacuum and purified as above.

The gas reacts also with tap grease under the influence of light. It was necessary, therefore, to work in diffused light and to surround the storage flasks with black paper.

All gases were repeatedly filtered through Schott's sintered glass filters. With the exception of CO_2 , the gases were all bubbled through a little liquefied gas. The non-fouling of the mercury in the barometer over long periods of time is attributed to these precautions, so that exceedingly reliable readings were obtained.

Results.

The results are shown in Tables I and II where P_0 is the corrected pressure referred to normal conditions, s is the weight of gas, L_p the gross weight of a litre and L_0 the corrected weight of a litre. As a most convenient practice, some corrections were directly done on the L_0 values.

Thus the vacuum reduction was made by the formula $v = \frac{L_0}{8.4} \times 0.0013$.

The compressibility coefficients per mm. deduced from our measurements were as follows: O_2 , 1.7×10^{-5} ; CO_2 , 1.8×10^{-5} ; C_2H_4 , 1.19×10^{-5} ; SO_2 , 9.01×10^{-5} ; SH_2 , 2.38×10^{-5} .

The numbers in Table I (1, 3, 4 and 5) were due to Moles and Roquero and determined in 1935; those in Table I (2 and 6) were obtained recently by Moles and (Miss) Toral in the same apparatus. The agreement between all the series is as good as possible and proves the inalterability of the apparatus.

TABLE I.—THURINGIAN GLASS.

Expt. No.	P_0	v	s	L_p	L_0
1. Oxygen under 760 mm.					
I	760.370	2564.19 ml.	3.66643	1.42916	1.42895
II	745.559	2564.19	3.59505	1.42917	1.42898
III	766.160	2392.72	3.44734	1.42917	1.42895
IV	755.575	2564.19	3.64327	1.42914	1.42894
V	756.580	2564.19	3.64804	1.42912	1.42892
				mean	1.428948 ± 0.000010
2. Oxygen under 570 mm.					
I	573.83	2393.51	2.58204	1.42876	1.42856
II	571.34	2393.51	2.57092	1.42880	1.42860
III	570.80	2393.51	2.56857	1.42884	1.42864
IV	570.01	2393.51	2.56491	1.42879	1.42859
				mean	1.428597 ± 0.000016
3. Oxygen under 506 mm.					
I	509.680	2564.04	2.45685	1.42878	1.42856
II	502.348	2564.04	2.42146	1.42876	1.42855
III	514.712	2564.04	2.48085	1.42863	1.42840
IV	509.950	2564.04	2.45809	1.42876	1.42854
				mean	1.428512 ± 0.00002

TABLE I.—THURINGIAN GLASS.—*Continued.*

Expt. No.	P_0 .	v .	s .	L_p .	L_0 .
4. Oxygen under 380.00 mm.					
I	393.908	4951.87	3.66643	1.42853	1.42829
II	386.245	4951.87	3.59505	1.42852	1.42829
III	370.397	4951.87	3.44734	1.42843	1.42828
IV	391.420	4951.87	3.64327	1.42854	1.42830
V	391.945	4951.87	3.64804	1.42850	1.42826
mean .				.	1.42828 ₄ ± 0.000006
5. Oxygen under 253.33 mm.					
I	263.995	4951.74	2.45685	1.42836	1.42810
II	260.210	4951.74	2.42146	1.42826	1.42802
III	266.591	4951.74	2.48085	1.42827	1.42800
IV	264.135	4951.74	2.45809	1.42832	1.42806
mean .				.	1.42804 ₅ ± 0.000017
6. Oxygen under 190 mm.					
I	192.08	4951.86	1.78747	1.42824	1.42802
II	193.13	2392.64	0.86832	1.42811	1.42789
III	190.36	4951.86	1.77149	1.42824	1.42802
IV	206.41	2392.64	0.92806	1.42817	1.42792
V	190.24	2393.33	0.85565	1.42823	1.42801
VI	193.52	2393.33	0.87033	1.42814	1.42792
mean .				.	1.42796 ₃ ± 0.00002 ₄
7. Ethylene under 760 mm.					
I	740.92	2392.97	2.94023	1.26034	1.26037
II	746.88	2392.97	2.96401	1.26039	1.26035
III	762.22	2392.97	3.02549	1.26064	1.26041
IV	764.83	2392.97	3.03573	1.26058	1.26033
V	754.90	2392.97	2.99610	1.26048	1.26033
VI	674.14	2392.97	2.67359	1.25956	1.26036
mean .				.	1.26035 ₈ ± 0.00001 ₁
8. Ethylene under 570 mm.*					
I	569.05	2392.82	2.25433	1.25826	1.25807
II	573.21	2392.82	2.27096	1.25833	1.25809
III	547.94	2392.82	2.17035	1.25804	1.25810
IV	576.71	2392.82	2.28488	1.25837	1.25809
V	567.61	2392.82	2.24857	1.25822	1.25805
VI	562.29	2392.82	2.22737	1.25815	1.25804
mean .				.	1.25807 ₈ ± 0.00001 ₀
9. Ethylene under 506.67 mm.*					
I	510.73	2392.85	2.02220	1.25756	1.25732
II	505.38	2392.79	2.00086	1.25749	1.25730
III	515.71	2392.79	2.04194	1.25761	1.25730
IV	504.45	2392.79	1.99719	1.25750	1.25732
V	433.18	2392.76	1.71380	1.25662	1.25730
VI	506.13	2392.79	2.00387	1.25752	1.25733
mean .				.	1.25731 ₃ ± 0.000006
mean for method (a)				.	1.257310
,, ,, (b)				.	1.257312

* Italicised figures were obtained with gas from method (b); the others by method (a).

TABLE I.—THURINGIAN GLASS.—*Continued.*

Expt. No.	P_0	v	s	L_p	L_0
10. Ethylene under 380 mm.*					
I	383.85	2392.79	1.51799	1.25607	1.25582
II	378.95	2392.79	1.49841	1.25591	1.25572
III	383.83	2392.79	1.51785	1.25602	1.25577
IV	356.76	2392.79	1.41047	1.25271	1.25579
V	382.06	2392.77	1.51072	1.25593	1.25571
VI	372.74	2392.77	1.47389	1.25595	1.25583
VII	379.09	2392.73	1.49901	1.25597	1.25578
VIII	360.07	2392.73	1.42362	1.25582	1.25586
IX	366.55	2392.73	1.44923	1.25579	1.25574
mean . . .					1.255780
					± 0.000017
mean for method (a)					1.25577
,, ,, (b)					1.25579
11. Ethylene under 253.33 mm.*					
I	230.74	2392.66	0.91112	1.25425	1.25431
II	256.74	2392.66	1.01394	1.25449	1.25420
III	250.62	2392.66	0.98976	1.25447	1.25425
IV	252.67	2392.66	0.99794	1.25452	1.25433
V	228.95	4951.91	1.87098	1.25420	1.25429
VI	254.48	2392.66	1.00507	1.25451	1.25430
mean . . .					1.254280
mean for method (a)					1.25431
,, ,, (b)					1.25427
12. Ethylene under 190 mm.*					
I	195.48	4951.86	1.59678	1.25368	1.25341
II	191.49	4951.86	1.56424	1.25373	1.25350
III	192.06	4951.86	1.56901	1.25381	1.25358
IV	193.22	4951.86	1.57834	1.25371	1.25346
V	192.60	4951.86	1.57337	1.25376	1.25351
VI	200.91	4951.86	1.64135	1.25384	1.25349
VII	194.42	2392.64	0.76737	1.25371	1.25344
VIII	191.85	4951.86	1.56737	1.25387	1.25363
mean . . .					1.253502
					± 0.00002
13. Sulphur dioxide under 760 mm.*					
II	764.48	2392.72	7.04640	2.92767	2.92658
III	759.04	2392.72	6.99498	2.92714	2.92654
IV	755.89	2392.72	6.96529	2.92684	2.92652
V	765.70	2392.72	7.05877	2.92775	2.92654
VI	760.23	2392.72	7.00618	2.92724	2.92653
VII	766.13	2392.62	7.06463	2.92783	2.92659
VIII	764.21	2393.74	7.04674	2.92760	2.92653
mean . . .					2.926547
					± 0.00001
Mean for method (a)					2.92655
,, ,, (b)					2.92653

* Italicised figures were obtained with gas from method (b); the others by method (a).

TABLE I.—THURINGIAN GLASS.—*Continued.*

Expt. No.	P_0 .	v .	s .	L_p .	L_0 .
14. Sulphur dioxide under 506.67 mm.					
I	510.61	2393.50	4.671315	2.90487	2.90377
II	507.73	2393.50	4.64429	2.90446	2.90362
III	508.47	2393.50	4.65115	2.90452	2.90357
IV	513.23	2393.50	4.69563	2.90513	2.90379
V	506.76	2393.50	4.63538	2.90443	2.90367
VI	508.54	2393.50	4.65204	2.90466	2.90374
VII	502.93	2393.62	4.60001	2.90408	2.90367
mean . . .					2.903690
					± 0.000028
mean for method (a)					2.90369
,, ,, (b)					2.90367
15. Sulphur dioxide under 380 mm.					
I	377.50	2393.44	3.43923	2.89291	2.89233
II	379.90	2393.44	3.46129	2.89305	2.89226
III	379.79	2393.44	3.46031	2.89309	2.89230
IV	381.85	2393.44	3.47917	2.89316	2.89220
V	385.67	2393.44	3.51444	2.89354	2.89223
VI	380.05	2393.44	3.46271	2.89311	2.89231
VII	380.85	2393.56	3.47022	2.89314	2.89227
mean . . .					2.892271
					± 0.000016
Mean for method (a)					2.89227
,, ,, (b)					2.89227
16. Sulphur dioxide under 253.33 mm.*					
I	254.49	2393.37	2.30965	2.88190	2.88090
II	249.14	2393.37	2.26074	2.88137	2.88085
III	252.76	2393.49	2.29378	2.88154	2.88069
IV	255.85	2393.49	2.32205	2.88183	2.88070
V	252.33	2393.49	2.28998	2.88164	2.88083
VI	251.49	2393.49	2.28226	2.88156	2.88083
VII	254.48	2393.49	2.30964	2.88184	2.88084
VIII	252.90	2393.49	2.27953	2.88151	2.88080
mean . . .					2.880805
					± 0.000020
mean for method (a)					2.88080
,, ,, (b)					2.88082
17. Sulphur dioxide under 190 mm.*					
I	187.47	2392.64	1.69735	2.87589	2.87515
II	197.22	2392.64	1.78618	2.87680	2.87518
III	190.50	2392.64	1.72492	2.87615	2.87513
IV	190.64	4951.86	3.57239	2.87600	2.87497
V	174.37	2392.64	1.57800	2.87455	2.87498
VI	191.92	4951.86	3.59694	2.87637	2.87522
mean . . .					2.875105
					± 0.000025

* Italicised figures were obtained with gas from method (b); the others by method (a).

TABLE II.—VOLUMETER B (JENA GLASS),

Expt. No.	P_0	v .	s .	L_p .	L_0 .
1. Oxygen (II) under 760 mm.					
I	754·82	2275·19	3·22950	1·428918	1·429000
II	749·30	4548·33	6·40856	1·429110	1·428937
III	763·49	2275·19	3·26656	1·429160	1·428963
IV	763·05	2275·19	3·26456	1·429110	1·428921
V	744·81	4548·33	6·37020	1·429120	1·428952
VI	765·95	2275·19	3·27695	1·429108	1·428910
VII	758·52	2275·19	3·24515	1·429103	1·428916
VIII	765·38	2275·19	3·27459	1·429143	1·428943
IX	748·79	2277·46	3·20673	1·428108	1·428954
mean . . .					1·428944 ± 0·000010
2. Oxygen (II) under 380 mm.					
I	377·78	4548·09	3·22950	1·42850	1·42832
II	382·12	4548·09	3·26656	1·42848	1·42829
III	381·89	4548·09	3·26456	1·42847	1·42828
IV	383·33	4548·09	3·27695	1·42850	1·42830
V	379·62	4548·09	3·24515	1·42847	1·42828
VI	383·06	4548·09	3·27459	1·42848	1·42828
VII	375·12	4548·09	3·20673	1·42848	1·42831
mean . . .					1·428294 ± 0·000005
3. Carbon dioxide (II) under 760 mm.*					
I	757·31	2275·19	4·48241	1·97712	1·976896
II	765·17	2275·61	4·53024	1·97732	1·97695
III	768·62	2275·61	4·53073	1·97736	1·976935
IV	761·35	2277·46	4·51112	1·97724	1·97694
V	762·98	2275·61	4·51717	1·97728	1·97695
VI	759·52	2275·61	4·496485	1·97720	1·97693
VII	760·36	2275·61	4·50151	1·97722	1·97694
mean . . .					1·976934 ± 0·000005
mean for method (a)					1·976934
,, ,, (b)					1·976935
4. Carbon dioxide (II) under 380 mm.*					
I	385·33	2275·50	2·27347	1·97055	1·97016
II	381·91	2275·50	2·25313	1·97044	1·97011
III	379·88	2275·50	2·24115	1·97043	1·97015
IV	380·31	2275·50	2·24367	1·97042	1·97013
V	379·88	2275·50	2·24111	1·97040	1·97011
VI	382·01	2275·50	2·25377	1·97048	1·97016
VII	383·94	2275·50	2·26517	1·97049	1·97014
mean . . .					1·970137 ± 0·000011
mean for method (a)					1·970137
,, ,, (b)					1·970137

* Italicised figures were obtained with gas from method (b); the others by method (a).

TABLE II.—VOLUMETER B (JENA GLASS).—*Continued.*

Expt. No.	P ₀ .	v.	s.	L _p .	L ₀ .
5. Sulphur dioxide (II) under 760 mm.*					
I	761.08	2275.61	6.67065	2.92721	2.92658
II	763.19	2275.61	6.68955	2.92739	2.92657
III	759.92	2275.61	6.66015	2.92706	2.92654
IV	759.23	2275.61	6.65534	2.92698	2.92652
V	756.84	2275.61	6.63258	2.92681	2.92656
VI	762.41	2275.61	6.68248	2.92729	2.92654
VII	762.26	2275.41	6.68058	2.92728	2.92654
mean . . .					2.92655
					± 0.00001
mean for method (a)					2.92655
,, ,, (b)					2.92654
6. Sulphur dioxide (II) under 380 mm.*					
I	380.31	2275.50	3.29413	2.89294	2.89229
II	380.80	2275.50	3.29847	2.89302	2.89233
III	380.83	2275.50	3.29866	2.89296	2.89227
IV	383.56	2275.50	3.32267	2.89328	2.89234
V	381.03	2275.50	3.29672	2.89308	2.89237
VI	383.68	2275.50	3.32363	2.89321	2.89226
VII	382.55	2275.29	3.31346	2.89315	2.89230
mean . . .					2.89231
					± 0.00002
mean for method (a)					2.89231
,, ,, (b)					2.89230

The agreement of the mean values by the two methods for ethylene, sulphur dioxide and for carbon dioxide proves furthermore the high purity of the gases employed.

Hydrogen Sulphide.—Some preliminary results obtained with H₂S are recorded.

Pure gas was prepared by hydrolysis of Al₂S₃, then cooled in a mixture of ice and salt, dried over P₂O₅, filtered through Schott's filter, bubbled and fractionated. In agreement with the observations of Cardoso and co-workers,⁷ after several fractionations a middle fraction which did not attack mercury was obtained. Moreover, to avoid a possible reaction by long contact, the measurements were undertaken by Regnault's method, using the same apparatus which had previously served for CO₂, N₂O and SiF₄.³ This was fitted with an Apiezon oil manometer between the barometer and the density bulbs, so allowing pressure equilibrium to be established without contact of the gas and mercury. Hydrogen sulphide dissolves to a very small extent and very slowly in Apiezon oil, so that no trouble arose in this way.

The density bulbs had the capacities: A = 580.955 ml. (after repair, A_n = 581.14). B = 454.735 ml. Corrections are made as usual.

Preliminary attempts to measure adsorption for H₂S show anomalous results, possibly due to reaction with the mercury of the apparatus. On account of its analogy in physical constants with CO₂ and HCl we can provisionally take the value 12×10^{-8} c.c. per cm.³ as the coefficient of adsorption.

Results corrected as usual are summarised in Table III in which the symbols have the same significance as above. The compressibility coefficient has been experimentally deduced as before.

* Italicised figures were obtained with gas from method (b); the others by method (a).

⁷ *J. Chim. physique*, 1912, 10, 504; *Gazzetta*, 1921, 51, 155.

TABLE III.

Expt. No.	ν .	P_0 .	s .	L_p .	L_0 .	Mean.
1. Hydrogen sulphide under 760 mm.*						
I	580.995	755.44	0.888605	1.53867	1.538537	1.538537
II	580.995	777.47	0.91473	1.53903	1.538357	1.538393
	454.735	777.47	0.71596	1.53909	1.538430	
III	580.995	774.41	0.91107	1.53893	1.538327	1.538323
	454.735	774.41	0.71306	1.53891	1.538320	
IV	580.995	745.86	0.87708	1.53823	1.538337	1.538423
	454.735	745.86	0.68654	1.53839	1.538510	
V	580.995	755.06	0.88806	1.53849	1.538367	1.538428
	454.735	755.06	0.69510	1.53860	1.538490	
VI	580.995	758.98	0.89276	1.53865	1.538427	1.538418
	454.735	758.98	0.69872	1.53862	1.538410	
VII	580.995	764.59	0.89945	1.53881	1.538457	1.538498
	454.735	764.59	0.70391	1.53868	1.538340	
VIII	580.995	767.95	0.90343	1.53887	1.538427	1.538413
	454.735	767.95	0.70707	1.53883	1.538400	
IX	454.735	762.55	0.70208	1.53877	1.538480	1.538480
X	581.140	756.99	0.89061	1.53860	1.538427	1.538463
	454.735	756.99	0.69691	1.53866	1.538500	
XI	581.140	755.33	0.88866	1.53862	1.538487	1.538483
	454.735	755.33	0.69535	1.53860	1.538480	
mean					1.538426 \pm 0.000012	
mean for (a)					1.538415	
mean for (b)					1.538436	

2. Hydrogen sulphide under 380 mm.*

I	454.735	374.07	0.34237	1.52968	1.52948	1.52948
II	580.995	383.79	0.44883	1.52976	1.52935	1.52938
	454.735	383.79	0.35130	1.52980	1.52941	
III	580.995	383.68	0.44874	1.52990	1.52949	1.529375
	454.735	383.68	0.35119	1.52979	1.52936	
IV	580.995	337.06	0.44094	1.52969	1.52942	1.52938
	454.735	377.06	0.34509	1.52971	1.52934	
V	580.995	375.36	0.43894	1.52965	1.52942	1.52943
	454.735	375.36	0.34355	1.52967	1.52944	
mean					1.529412 \pm 0.000016	
mean for (a)					1.529420	
mean for (b)					1.529406	

As appears from Table IV. the probable errors in the mean values are somewhat fortuitous. There is no strict proportionality between the errors and the measuring pressures. We conclude, then, that the limit of accuracy 10^{-5} is practically reached in practice for every gas at every pressure.

TABLE IV.

p .	O ₂	C ₂ H ₄	SO ₂	O ₂	CO ₂	SO ₂	SH ₂
1.000	0.70	0.85	0.35	0.69	0.26	0.35	0.78 $\times 10^{-5}$
0.750	1.14	0.80	—	—	—	—	—
0.667	1.40	0.50	0.90	—	—	—	—
0.500	0.40	1.35	0.55	0.35	0.55	0.70	1.03
0.333	1.20	1.40	0.70	—	—	—	—
0.250	1.65	1.60	0.85	—	—	—	—

* Italicised figures were obtained with gas from method (b); the others by method (a).

Adsorption Correction.

Correction for adsorption on the glass walls of density flasks has been experimentally determined for every gas in our Institute by Crespi.⁸ The corrections for different pressures expressed in grams per litre are given in Table V.

TABLE V.

	$p = 1.0000.$	$0.50000.$	0.25000 atm.
Thuringian glass.			
O ₂	2.0	2.7	$3.2 \times 10^{-5} \text{ gr.}$
CO ₂	6.1	9.1	13.2
C ₂ H ₄	2.8	3.4	4.4
SO ₂	30.0	41.0	57.0

Jena glass.

CO ₂	1.5	$2.2 \times 10^{-5} \text{ gr.}$
SO ₂	13.8	23.2

Comparison has already been made⁴ between various molecular weights of CO₂ and various atomic weights of carbon, as deduced of the limiting density and employing uncorrected and corrected numbers which lead to differences as great as $C = 12.012$ and 12.007 . In order to ascertain the accuracy of the

adsorption correction, a direct comparison can be made (Table VI) of the new results for CO₂ and SO₂ with the previous ones deduced by Moles and Toral for CO₂, employing volumeter A with both density bulbs of Thuringian glass and volumeter B of Jena glass and with corrected and uncorrected values.

TABLE VI.

Gas.	Method.	$L_p.$	
		Corrected.	Uncorrected.
CO ₂	{ Bulb Volumeter B	1.976938	1.977038
		1.976934	1.976952
		0.000004	0.000086
SO ₂	{ Volumeter A Volumeter B	2.926547	2.926850
		2.926550	2.926690
		0.000003	0.000160

in the volumeter B of Jena glass and capacity from about 2400-4500 ml. is very significant and proves the complete absence of systematic errors.

Density as a Function of Pressure.

As has been established above, Berthelot's rule of the limiting densities applies, within the limits of accuracy required in atomic weight measurements, only if linear extrapolation of the limiting values holds strictly good for all gases over the range of pressure investigated. From preceding results the relationship between L_p and p can be expressed by the equations shown in Table VII.

Whatever be the extreme cases of a *less compressible* gas, oxygen and an *exceedingly compressible* one, so far as concerns sulphur dioxide, no differences in behaviour were remarked. Ethylene and sulphur dioxide are of the same type as CO₂, NH₃ and SiF₄, with which we have dealt in previous papers. For all, the $L_p - p$ curve is linear within the limits of

⁸ A summary of this work is given in *Bull. Soc. chim. Belgique*, 1938, 47, 405.

our experimental error, which is of the order of 1 in 100,000 on an individual ratio. Consequently, $L_p = a + bp$, where a is the limiting density.

TABLE VII.

p	L_p obs.	L_p calc.	
Oxygen (I) $L_p = (1.427619 \pm 0.000005) + 0.0001326 \cdot p$.			
1.00000	1.428948	1.428945	-0.3×10^{-5}
0.75000	1.428600	1.428612	+ 1.2
0.66667	1.428512	1.428503	- 0.9
0.50000	1.428284	1.428282	- 0.2
0.33333	1.428045	1.428061	+ 1.6
0.25000	1.427963	1.427950	- 1.3

Ethylene , $L_p = (1.251223 \pm 0.000002) + 0.009134 \cdot p$.			
1.00000	1.260359	1.260357	-0.2×10^{-5}
0.75000	1.258073	1.258073	± 0.0
0.66667	1.257312	1.257312	± 0.0
0.50000	1.255780	1.255790	+ 1.0
0.33333	1.254280	1.254267	- 1.3
0.25000	1.253502	1.253506	+ 0.4

Sulphur dioxide , $L_p = (2.857957 \pm 0.000005) + 0.068593 \cdot p$.			
1.00000	2.926547	2.926550	+ 0.3
0.66667	2.903690	2.903685	- 0.5
0.50000	2.892271	2.892253	- 1.8
0.33333	2.880805	2.880821	+ 1.6
0.25000	2.875105	2.875105	± 0.0

Discussion of the Results.

As stated above, molecular weights of gases in relation to our oxygen system are deduced according to the rule of the limiting densities of Berthelot from the simple equation

$$M' = 32.000 \cdot r_0,$$

where 32.000 is the conventional molecular weight of oxygen and r_0 is the ratio of the limiting densities $L_{\text{lim}} : L^\circ_{\text{lim}}$ or the value extrapolated to $p = 0$ from the partial ratios of the L_p values. We thus obtain from the above the values given in Table VIII.

TABLE VIII.

p .	r_p .	r_0 .	r_p .	r_0 .
Ratio $\text{C}_2\text{H}_4 : \text{O}_2$ (I).			Ratio $\text{SO}_2 : \text{O}_2$ (I).	
1.00000	0.882020		2.04804	
0.75000	0.880631	0.876464		
0.66667	0.880154	0.876422	2.03267	2.00193
0.50000	0.879223	0.876426	2.02500	2.00196
0.33333	0.878320	0.876470	2.01734	2.00198
0.25000	0.877824	0.876425	2.01343	2.00189
mean		0.876441		2.00194
$r_0 = L_{\text{lim}} : L^\circ_{\text{lim}} =$		0.876441		$= 2.00193$
Ratio $\text{CO}_2 : \text{O}_2$ (II).			Ratio $\text{SO}_2 : \text{O}_2$ (II).	
1.00000	1.383492		2.04805	
0.50000	1.379362	1.375234	2.02501	2.00197
$r_0 = L_{\text{lim}} : L^\circ_{\text{lim}} =$		1.375231		2.00196
Ratio $\text{H}_2\text{S} : \text{O}_2$.				
1.00000	1.07662			
0.50000	1.07080	1.06498		
$r_0 = L_{\text{lim}} : L^\circ_{\text{lim}} =$		1.06497		

For the molecular weights it follows

$$\begin{array}{ll} M(\text{C}_2\text{H}_4) = 28.046 & M(\text{CO}_2) = 44.0074 \\ M(\text{SO}_2)^1 = 64.062 & M(\text{SO}_2)^2 = 64.063 \\ M(\text{SH}_2) = 34.079 & \end{array}$$

and therefore for the atomic weights

$$\begin{array}{ll} \text{C} = 12.007 (\text{C}_2\text{H}_4) & \text{S} = 32.062 (\text{SO}_2) \\ \text{C} = 12.0074 (\text{CO}_2) & \text{S} = 32.063 (\text{SO}_2) \\ & \text{S} = 32.063 (\text{SH}_2) \end{array}$$

as compared with previous values obtained from the limiting densities from CO and CO₂:

$$\text{C} = 12.0064 \text{ and } \text{C} = 12.007$$

The general mean of the four different values for carbon leads to

$$\text{C} = 12.007 \pm 0.0002,$$

which is identical with the reduced physical value on the basis of the most recent results on isotopic weights of carbon,⁹ the relative abundance $\text{C}^{12} : \text{C}^{13} = 99.3 : 0.7$ as accepted in the 3rd Report of the International Committee on Atomic Weights for 1938 and with the most probable conversions factor 1.000275.¹⁰ It is somewhat lower than the accepted value in the International Table $\text{C} = 12.010$. The value for sulphur $\text{S} = 32.063$ agrees with the accepted international one and agrees also with the physical value referred to chemical scale $\text{S} = 32.064$, when the abundance ratio for isotopes, as found recently by A. O. Nier, is taken in account. The error in the third decimal figure should not exceed 1 or 2 units.

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⁹ Aston, *Proc. Roy. Soc., A*, 1937, 163, 591; *Nature*, 1938, 1096.

¹⁰ R. Whytlaw-Gray, *Annual Reports*, for 1938, 125.

THE ADSORPTION ERROR IN THE DETERMINATION OF GASEOUS DENSITIES AND THE ADSORPTION OF GASES ON VITREOUS SILICA.

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In the determination of the densities of gases with the object of evaluating exact molecular weights it is important to consider carefully the possibility of errors due to adsorption. Although on glass surfaces this effect is small for the permanent gases, Moles contends that with modern refinements of technique it is not entirely negligible. However, for gases of this class when weighed in litre bulbs the adsorption error is of the order of only a few parts in 10⁵. For more easily liquefiable gases this error is very appreciable and without correction the results

lead, on extrapolation, to unreliable values for the limiting densities and molecular weights. Thanks, however, to the careful investigations of Crespi² and of Moles¹ and Crespi, who have measured the adsorption of many gases on surfaces of glass closely similar to those of the bulbs used for densities, it is now possible to apply reliable corrections and to calculate the limiting densities of easily liquefiable gases with greater accuracy than has been possible hitherto. Moles and his collaborators have also observed that adsorption on Jena glass is distinctly smaller than on soft soda glass, but no corresponding data are available either for pyrex glass or vitreous silica. Adsorption on the latter material has never been adequately investigated in the pressure-temperature region in which the physical constants of gases are measurable with high precision.

Although the present work furnishes an answer to the question whether vitreous silica is markedly superior to glass for highly accurate gasometric work in general its real object was to investigate possible adsorption errors in the silica buoyancy balance when used for comparing the densities of gases.

Previous work at Leeds has shown that adsorption on surfaces of vitreous silica is small. For instance, quartz vessels can be weighed easily and quickly on delicate microbalances whereas glass vessels only attain equilibrium slowly. The attempt some years ago to weigh the adsorbed layer of CO₂ and of air on a silica surface of 40 cm.³ gave negative results even though a microbalance of a sensitivity of 2×10^{-8} gram was used. Coppock and Whytlaw-Gray⁴ found in measuring the coefficients of expansion of some liquefiable gases at a series of pressures that the results in silica, when extrapolated, led to the theoretical value for the coefficient at zero pressure, whilst when glass vessels were used extrapolation yielded values undoubtedly too high, and a calculation based on the assumption that adsorption on silica was negligibly small gave values for the adsorption of the various gases on glass in conformity with Moles' data. On the other hand, limiting densities determined by means of silica buoyancy balances with equal surfaces on the two ends of the beam gave with certain gases results which were clearly vitiated by adsorption errors.⁵

These observations threw doubt on the reliability of purely geometric compensation of surface moments on the two sides of the balance beam and led to a more trustworthy procedure in which the highly absorbable gas sulphur dioxide was used to determine whether really effective surface compensation had been attained; the assumption being made that if adsorption had been eliminated for sulphur dioxide the balance could be relied on to give highly accurate results when used for less adsorbable gases.

At an international discussion held at Neuchatel in 1938⁶ the opinion was expressed that in spite of this procedure the results furnished by the buoyancy balance might still be affected by errors of adsorption

¹ E. Moles, *Bull. Soc. Chim. Belg.*, 1938, 47, 416.

² M. Crespi, *ibid.*, 1938, 47, 423; for complete references in *Anal. Fis. Quirn.*, 1926-36.

³ F. W. Clulow, Ph.D. Thesis, Leeds, 1932.

⁴ J. B. M. Coppock and R. Whytlaw-Gray, *Proc. Roy. Soc. A*, 1934, 143, 487.

⁵ W. Cawood and H. S. Patterson, *Phil. Trans. A*, 1936, 236, 84.

⁶ *Les Determinations physico-chimiques des Poids Moleculaires et Atomiques des Gaz. Institut. Internat. Intellect. Co-operat.*, Paris, 1938.

and that it would be desirable to study carefully with a series of gases adsorption on vitreous silica.

This has now been done and it will be seen that adsorption on clean surfaces of this material is very small and a great deal less than adsorption on glass surfaces for the same gases.

Experimental.

The experimental method adopted is similar to that used to measure the volume of HCl adsorbed on glass by Burt and Gray⁷ in 1918.

Essentially it consists in displacing gas at constant pressure from a glass bulb or cylinder by mercury and then exposing the surface on which the gas is adsorbed to a high vacuum by lowering the mercury again. On filling the vessel once more with mercury the adsorbed gas is driven into a fine capillary and its volume measured. This operation can be repeated a number of times until no more gas is collected in the capillary.

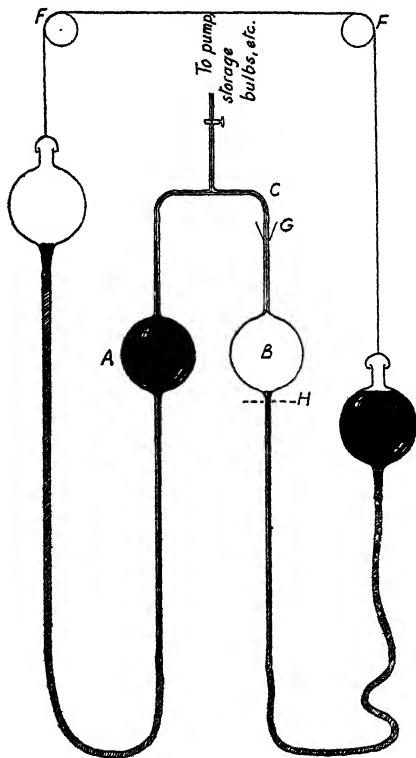


FIG. 1.

The essential parts of the apparatus are shown in the accompanying sketch (Fig. 1). In this, to avoid complication, the gas traps at the junction of the rubber tubing and the glass fall tubes as well as the silica glass joints and drying tubes above the mercury reservoirs have been omitted. A and B are special bulbs of clear vitreous silica of about 400 c.c. capacity connected above by the fine silica capillary C and joined by means of a ground silica glass joint to the leading tubes, gas storage bulbs, MacLeod gauge and evacuating pumps. Below the bulbs were attached by cemented ground connections (not shown) to two long fall tubes of glass carrying at their base two air traps (not shown) and joined by special rubber tubing to two mercury reservoirs. The latter were suspended by a strong cord passing over the two pulley wheels FF, so that the raising of one reservoir lowered the other by the same amount and enabled the gas to be displaced from bulb A to bulb B at constant pressure. The actual pressure at which the gas was displaced could be altered by varying the length of the cord.

In carrying out a determination, one of the bulbs, say A, was filled with mercury and the other with gas at a given pressure. After a suitable interval the gas was slowly displaced from B to A by raising and lowering the reservoirs when attached to the cord and pulleys. The mercury in B was now raised to fill the capillary and the thread of mercury frozen by means of solid CO₂ and acetone in the filter paper cone G. The reservoir of B was then detached from the cord and lowered until the mercury

⁷ F. P. Burt and R. W. Gray, *Trans. Faraday Soc.*, 1911, 7, 31.

stood at H, thus exposing the walls of B to a high vacuum. On raising this reservoir again the evolved gas was compressed into the calibrated capillary below the frozen mercury and its volume measured. By thawing the mercury the thread of gas could be pushed over in bulb A and the process repeated after freezing the mercury thread again.

Very special precautions were taken to ensure (a) the purity of the mercury and the avoidance of contamination by contact with the rubber tubing or in the subsequent operations; (b) the cleanliness and absence of films on the interior surfaces of the silica bulbs. (a) The mercury was first purified and dried by standard methods of agitation with mercurous nitrate solution, followed by dessication by aspiration of dust-free air. It was then agitated with redistilled chloroform and finally dried in an air stream and filtered through a fritted filter of Jena glass. The rubber tubing was unvulcanised and of the translucent variety employed for surgical purposes. After removal of dust from the interior by brushing out, washing and drying, it had no visible action on mercury even after months of contact. (b) The silica bulbs were treated with a warm mixture of perchloric acid and magnesium perchlorate, washed with distilled water, dried in dust-free air, and heated to dull redness. The whole of the apparatus after it was set up was evacuated down to a pressure of 1/1000 mm. and allowed to stand in presence of phosphorus pentoxide for some days before use. The gases used were highly purified specimens, most of them having been used previously for atomic weight work. The behaviour of the silica surfaces proved very different to that found for similar glass surfaces by Gray and Burt.⁷ Not only was the quantity of gas collected much smaller but it was given off completely in one operation whilst the gas from glass surfaces came off slowly, each raising and lowering of the mercury yielding a smaller and smaller increment and finality was only reached after some hours. Again the volume of gas obtained at the same pressure with the silica surfaces was perfectly constant within the limits of experimental error and did not seem to depend in any way on the previous history or treatment of the vessel or on the gases with which it had been in contact. Thus with ethylene, which was the first gas introduced, measurements were repeated after the apparatus had been used for a series of other gases, and values in close agreement with those found initially were obtained.

The objection might be made to this method that the volume of the gas measured is not due entirely to adsorption but is augmented by gas trapped in depressions and irregularities of the silica surface when the mercury rises. This would make the volume attributed to adsorption too large, but though no definite proof can be advanced that this effect is not present to some extent the results as a whole with different gases show at least that this trapped gas effect must be small in the case of the more adsorbable gases.

The following gases were studied: CO_2 , C_2H_4 , N_2O , O_2 , A, N_2 , CO , SO_2 . Full experimental results are given in Tables I and II for SO_2 and CO_2 . For the others, the figures quoted (in Table III) are from the smoothed curves.

The data were obtained at room temperature, 21°C . The internal surface of the bulb was 271 sq. cm.

The results were reproducible. For instance, Experiment 2 (Table I) was repeated three times allowing the gas to remain for 30, 60 and 60 minutes in the bulb and then desorbing for 20, 20 and 30 minutes. Each time the same result was obtained. In Experiment 4 the gas on one occasion remained in contact with the surface of the bulb for 16 hours and this gave the same result as a contact of 1 hour. Experiments 1, 6 and 7 were made at a later date after several other gases had been in the apparatus. It is clear that adsorption and desorption are rapid and quite unlike the corresponding behaviour on glass surfaces.

It will be noticed that of all these gases oxygen is least adsorbed.

TABLE I.—ADSORPTION OF CARBON DIOXIDE.

Exp.	Pressure of Gas in Bulb (mm.).	Volume of Gas Desorbed (in cub. mm. at 760 mm. and 21° C.).	Volume of Gas Desorbed per sq. cm. (at 760 mm. and 21° C.).
1	669	0.363	1.34×10^{-6} C.C.
2	592	0.341	1.26
3	522	0.311	1.15
4	348	0.223	0.83
5	251	0.183	0.68
6	152	0.130	0.48
7	84	0.080	0.29

TABLE II.—ADSORPTION OF SULPHUR DIOXIDE.

Exp.	Saturation Pressure of Gas (mm.).	Volume of Gas Desorbed (in cub. mm. at 760 mm. and 21° C.).	Volume of Gas Desorbed per sq. cm. (at 760 mm. and 21° C.).
1	812	3.11	11.5×10^{-6} C.C.
2	747	2.88	10.6
3	624	2.74	10.1
4	572	2.57	9.5
5	415	2.16	8.0
6	258	1.79	6.6
7	165	1.52	5.6
8	128	1.36	5.0
9	103	1.10	4.1
10	48	0.751	2.8
11	27	0.623	2.3

TABLE III.

TABLE III.—THE VOLUME OF VARIOUS GASES ADSORBED IN C.C. $\times 10^6$ PER SQ. CM. OF SURFACE (AT 760 M.M. AND 21° C.) AT DIFFERENT PRESSURES.

Pressure (mm.).	760	700	600	600	400	300	200	200	50	30
Gas.										
SO ₂ .	11.0	10.6	9.8	9.0	8.1	7.2	6.0	4.2	2.7	1.9
N ₂ O .	1.61	1.53	1.38	1.22	1.04	0.82	0.59	0.31	0.16	0.096
C ₂ H ₄ .	1.50	1.46	1.35	1.22	1.04	0.84	0.60	0.33	0.17	0.10
CO ₂ .	1.45	1.39	1.27	1.12	0.96	0.77	0.56	0.30	0.16	0.096
N ₂ .	0.74	0.69	0.60	0.51	0.42	0.33	0.23	0.11	0.057	0.034
CO .	0.44	0.42	0.37	0.32	0.27	0.21	0.15	0.075	0.038	0.022
A .	0.42	0.40	0.36	0.31	0.26	0.20	0.14	0.071	0.037	0.022
O ₂ .	0.20	0.19	0.18	0.16	0.14	0.11	0.08	0.041	0.022	0.013

These results—given in Table III—are shown graphically in Fig. 2.

Also that CO is less adsorbed than nitrogen. The adsorption curves of volume adsorbed against pressure are of the usual type and up to about 400 mm. follow closely Freundlich's adsorption formula.

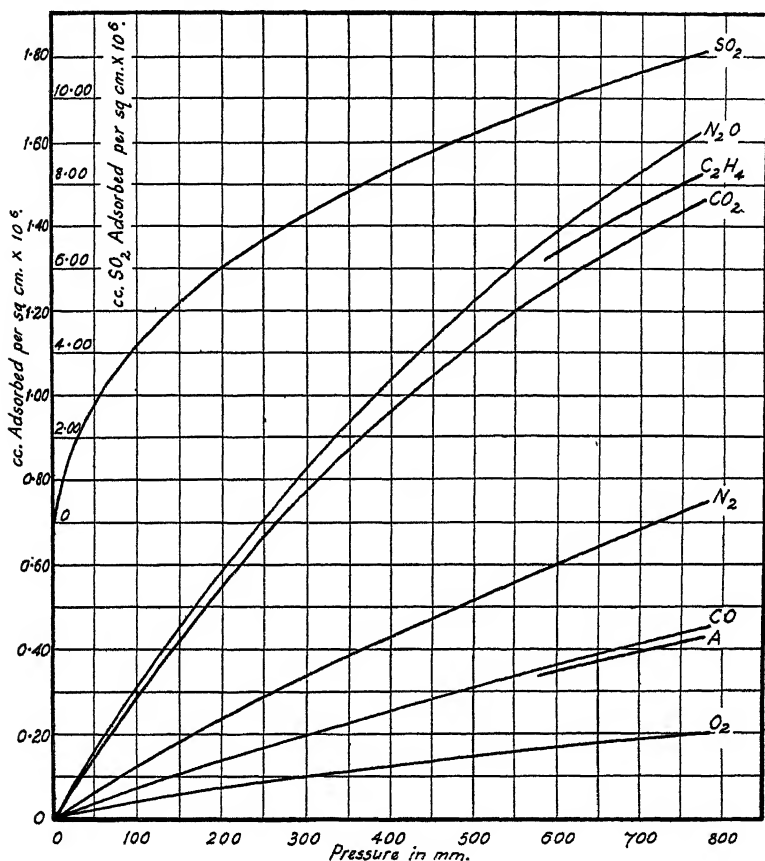


FIG. 2.

It is of interest to compare these data with the corresponding data obtained by Moles for the same gases on glass. In Table IV the results obtained at 760 mm. and room temperature are given :

TABLE IV.

Gas.	Silica Surfaces (c.c./sq. cm. 760 and 21° C.).	Soda Glass (c.c./cm. ² 760 and 15° C.).	Jena Glass.
SO ₂ .	11.0 × 10 ⁻⁶	290 × 10 ⁻⁶	130 × 10 ⁻⁶
N ₂ O .	1.61 × 10 ⁻⁶	63	
C ₂ H ₄ .	1.51 × 10 ⁻⁶	63	
CO ₂ .	1.44	89	20 × 10 ⁻⁶
N ₂ .	0.74		
CO .	0.44	23	
A .	0.42		
O ₂ .	0.20	41	

It is clear that adsorption on silica surfaces is many times less than on glass. Thus a surface of ordinary glass adsorbs twenty-six times and a Jena glass surface twelve times as much SO_2 as a surface of vitreous silica. In the case of the other gases the disproportion is even more marked.

In both sets of measurements the data apply only to the gas evolved from the surface when the pressure is reduced to about 0.001 mm. It is the layer which varies with pressure. On silica this layer does not cover completely the geometrical surface. For example, the amount of gas adsorbed with SO_2 is about one half the quantity required for a monomolecular layer, *i.e.* only 50 per cent. of the geometrical surface is covered. With oxygen the percentage covered is roughly 0.7 per cent. and with CO_2 6 per cent.

On ordinary glass from Moles' measurements the SO_2 layer is 13 molecules thick, the CO_2 layer nearly 4 molecules, and the oxygen layer a little greater than 1 molecule.

It may be questioned, however, whether the removable layer represents the whole of the gas on the surface and whether there is not as well a fixed layer which is not removed in a high vacuum. This fixed layer, if present, would not affect the correction for adsorption applied by Moles and his co-workers when weighing gases in bulbs. It might, however, influence the data obtained with the microbalance where the buoyancy bulb is exposed alternately to the two different gases, the balancing pressures of which are under comparison. In this case the second gas might displace the fixed layer of the first and the adsorption might be much greater than that for the removable layer alone.

It is hence a matter of importance to determine whether on vitreous silica surfaces there is a fixed layer of gas which is not evolved at low pressures in addition to the adsorbed gas which we have measured.

It is not easy to settle this question by the method described above. Attempts, however, were made to see if any further gas could be obtained from the interior surface of the silica bulb by heating after the removable layer had been eliminated by a long exposure to a high vacuum. Accordingly, at the end of the series of experiments with the various gases nitrogen was introduced again into the bulb and the gas adsorbed at pressures of 255 mm. and 621 mm. measured, values of 0.23×10^{-6} and 0.66×10^{-6} c.c. per sq. cm. were obtained in good agreement with the earlier values. It was therefore concluded that there had been no alteration in the surface by contact with other gases. After removal of the nitrogen the bulbs was heated to redness in a blowpipe flame and the walls subjected at the same time to the action of the silent electric discharge for thirty minutes. Each time this was done small amounts of gas were given off at a steady rate and it was found impossible to get the bulb free from gas. Another set of experiments in which no nitrogen was used gave closely similar results and it became evident that the gas collected was hydrogen which diffused slowly through the red hot walls from the blowpipe flame. It might be contended that since the amounts of gas in the blank experiments and with nitrogen were in agreement that the possibility of a fixed layer of nitrogen was excluded. Anyway had all the gas evolved been nitrogen in the first set of experiments and hydrogen in the second the amount would have been far short of a monolayer. More direct evidence of the non-existence of a fixed layer underneath a removable layer of gas was obtained by direct weighing of the adsorbed film with the help of a delicate microbalance. By this method it was not found possible to measure quantitatively the films of less adsorbable gases such as nitrogen, carbon monoxide, or air, but the adsorption and desorption of SO_2 at 21° C. was studied in some detail. A complete account of this work will be published shortly. With this gas it was found that the adsorbed film could be removed completely by exposure to a high vacuum for some hours and that when desorption ceased the balance returned to its original zero. For this gas at least there is obviously no

fixed layer at all comparable in amount to the removable gas layer. It seems likely that this statement is true also for other gases. Another point of interest is the approximate agreement between the volumes of adsorbed gas given by the displacement and microbalance methods. The former gave 11.0×10^{-6} c.c. per cm.² and the latter 8.7 after saturation at 1 atm. in spite of the possible difference in the silica surfaces. In the displacement method adsorption was on the interior of a bulb of moulded silica whilst in the microbalance method the surface was composed of thin laminæ obtained from very thin walled bulbs. Results obtained with the microbalance for N₂ and CO₂ at atmospheric pressure, though not very accurate, were in approximate agreement with the data in this paper. It may be concluded then that the displacement method gives reliable results which are not affected to any great extent by (a) trapped gas, (b) adsorption on mercury.

Our experience shows that adsorption varies very little with the treatment and past history of any particular surface of silica. For instance, contact with other gases, heating to redness and application of the silent electric discharge did not alter the adsorption measured by the displacement method. Again the silica laminæ used as the adsorption surface on the microbalance were frequently heated to redness for many hours and practically the same values obtained before and afterwards. Different silica surfaces do, however, show a difference in the amount of gas they adsorb. Before the experiments described were commenced similar experiments were made by one of us and Dr. Cawood, using instead of bulbs, cylinders of silica of approximately the same surface. These, though apparently of clear silica, showed a slight bloom or opalescence on the interior surfaces when viewed in a strong beam of light from the arc. When adsorption was measured for SO₂, C₂H₄ and CO₂ and N₂, values six to seven times as large as those in this paper were obtained. This is an observation of some practical interest for in making silica microbalances the silica volatilised by the oxy-coal gas flame is apt to deposit on adjacent cooler surfaces of silica and to form a thin bloom or film.

It is clear that the presence of only a slight film may greatly magnify adsorption errors. Experiments have also been made in another cylindrical apparatus the interior surfaces of which were free from bloom. Data were obtained for C₂H₄, CO₂, SO₂, N₂ and O₂, and though the amounts of gas adsorbed were appreciably larger than those quoted in this paper, the form of the isothermals and the relative quantities adsorbed of the several gases were closely similar. There seems to be little doubt that where clean silica surfaces free from bloom are involved adsorption does not vary very much from one particular specimen to another.

On the basis of these results we can now assess the probable errors produced by adsorption in the molecular weights of gases determined by means of the silica microbalance by the method of limiting pressures.

In most cases oxygen was taken as the comparison gas and the pressures at which the balance set to the zero point in oxygen and another gas were measured. Our figures show that adsorption with oxygen is far too small to cause an appreciable error. Hence when an adsorbable gas X is compared with oxygen the ratio of the balancing pressures at equal densities, *i.e.* p_{O_2}/p_X will be smaller than it would have been had adsorption been absent. The effect of adsorption on the buoyancy bulb of the balance will be to give too low a value for this ratio and hence too low a value for the molecular weight of X when the ratio values are extrapolated to zero pressure. As the pressure falls, adsorption over the pressure range comprising the measurements decreases more slowly than density so that the error will be greater at the lower pressures

Consider, for example, the results obtained by Cawood and Patterson⁸ in comparing the balancing pressures of sulphur dioxide. By successive small adjustments of the surfaces on opposite ends of the beam they finally obtained the values shown in column 2 of Table V, and since these values led on extrapolation to a molecular weight of sulphur dioxide, 64.058, in close accordance with the most reliable stoichiometric data, they concluded that the balance was satisfactorily compensated for adsorption and that the values obtained by its use with less adsorbable gases would be highly accurate. At the time the adsorption of SO₂ on silica had not been measured, but the results in this paper show that this conclusion was fully justified, and that Cawood and Patterson's method of eliminating adsorption errors was sound.

Assuming, then, that these ratios are not affected by adsorption errors, it is of interest to

TABLE V.

p_{O_2}	Compensated p_{O_2}/p_{SO_2} (no adsorption).	Uncompensated. p_{O_2}/p_{SO_2}
417.564	2.01154	2.01141
226.940	2.00710	2.00692
(zero)	2.00182	(2.00157)

TABLE VI.

Pressure.	Weight of gas adsorbed. Weight of gas displaced. For Bulb of 1.7 cc. at 21° C.
760 mm.	0.452×10^{-4}
600	0.513
400	0.633
300	0.746
200	0.943
100	1.32
50	1.67
30	1.98

calculate the amount by which the ratios p_{O_2}/p_{SO_2} would have been diminished if the buoyancy bulb had not been compensated at all. This can be done by finding what fraction the weight of adsorbed gas is of the weight of the gas displaced at various pressures. For a sphere of 1.7 c.c. (the volume of the bulb used) we find the ratios shown in Table VI.

The ratios in column 3 in Table V were calculated from these data. On extrapolation we get for the molecular weight of sulphur dioxide 64.050 instead of 64.058, so that adsorption causes an error of 1 part in 8000 in the molecular weight and 1 part in 4000 in the atomic weight of sulphur. This is the error that would be produced if the surface of the buoyancy bulb adsorbed SO₂ to the same extent as the surface used for the adsorption experiments. Had the surface of the bulb, however, been covered with a film of volatilised silica adsorption would have been many times greater. Assuming it to be seven times as large, a figure found experimentally with the first cylindrical displacement apparatus, the molecular weight of SO₂ and the atomic weight of sulphur would have been found to be respectively one part in 1300 and 1 part in 650 too small, a very gross error in work of this character. Actually, on examining the balance used by Cawood and Patterson both the buoyancy bulb and its compensating silica cover glass were found to be covered by a white film of silica deposit. The presence of this probably accounts for the difficulty these workers experienced in accurately compensating the surfaces. It also affords a likely explanation of the high values obtained for the molecular weights of ethylene and nitrous oxide before the final surface compensation with SO₂ was made.

⁸ *Loc. cit.*⁵ p. 85.

On clean surfaces of vitreous silica the adsorption even of nitrous oxide and ethylene is so small that at pressures of a few hundred mm. the adsorption error on a bulb of 1.7 c.c. would be imperceptible. It is evident, then, that if care is taken in selecting the bulb and its counterweight, errors of adsorption can even with gases like SO_2 be reduced to negligible dimensions. A surface compensation on the two sides of the balance within 20 per cent. should not give rise with SO_2 to an error greater than 1 part in 40,000 in the molecular weight. Thus the adsorption error with SO_2 on a properly designed silica buoyancy balance is much smaller than it is in a glass bulb of 1 litre capacity as used by Moles for density determinations by the classical method.

No mention has so far been made in this paper of the behaviour of hydrogen. Originally the late Dr. Burt and one of us (R. W.-G.) made some measurements with hydrogen and other gases in the same glass apparatus, used afterwards for hydrogen chloride. At the time the results were regarded only as preliminary values and were not published, but of the several gases examined hydrogen gave the smallest adsorption in the displacement apparatus. With silica a similar result was expected, but on making the experiments we found to our surprise that astonishingly large values were obtained of the same order of magnitude as those found for sulphur dioxide. Moreover, it was difficult to get consistent results and the amount of gas collected was found to vary with the period of contact with the surface and the time allowed for desorption.

When the silica was heated, hydrogen was slowly given off again in a vacuum and quite large amounts could be collected which were in the aggregate very much greater than the hydrogen diffusing in the same period through the walls of the vessel from the blowpipe flame. It is evident that the adsorption of hydrogen on vitreous silica is quite anomalous. Further experiments with this gas are in progress.

Although no experiments were made with helium by the methods described it is worth while recording that this gas slowly penetrates vitreous silica even at 0°C . Some years ago Dr. Wild,⁹ working in these laboratories, attempted to compare directly the densities of hydrogen and helium using a silica buoyancy balance. He found it impossible to obtain a constant zero in helium, the balance moving steadily in one direction whenever it was surrounded with this gas whilst in hydrogen it remained constant. It was obvious that the diffusion of helium through silica, which is so marked at higher temperatures, is appreciable at 0°C . Jacqueroed has noted a similar effect at room temperature.

In conclusion, it is evident that adsorption even of easily liquefiable gases on clean surfaces of vitreous silica is for the majority of gases very much smaller than on glass surfaces.

The use of silica vessels in future work would reduce to negligible proportions uncertainties due to adsorption effects in the determination of compressibilities, coefficients of expansion and densities of gases.

The results also confirm the reliability of the limiting pressure method for comparing the exact molecular weights of gases with the silica buoyancy microbalance.

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⁹ W. Wild, Ph.D. Thesis, Leeds, 1930.

APPARENT MOLAL VOLUMES OF STRONG ELECTROLYTES IN AQUEOUS SOLUTIONS.

BY M. K. SRINIVASAN AND B. PRASAD.

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Masson¹ showed empirically that the apparent molal volume ϕ , of a strong electrolyte is a linear function of the square root of its concentration c , expressed in gram moles per litre; $\phi = \phi_0 + K\sqrt{c}$, where ϕ_0 and K are constants characteristic of each solute and temperature. Later this equation was deduced from the interionic theory by Redlich and Rösenfeld,² according to whom the value of the constant K should be the same for all strong electrolytes of the same valence type at extreme dilutions. The validity of this theory has been examined by many workers.³ But their measurements do not generally extend to very low concentrations. Not much work seems to have been done so far at 35° C. So it was thought desirable to study the apparent volume changes of some strong electrolytes of the uni-univalent type in dilute solutions at this temperature. With this object the densities of aqueous solutions of sodium nitrate, sodium chloride, potassium nitrate and potassium chloride were measured. Some existing data at other temperatures were also examined.

Experimental.

The thermostat has been described in a previous communication.⁴ Density determinations were made at 35° ± 0.005 C. with a pyknometer of about 63 c.c. capacity, having capillary ends with a mark on each end to which the liquids were adjusted after they had attained the temperature of the bath. A platinum syringe was used for adjusting the levels. To prevent loss of liquid due to evaporation, the pyknometer was fitted up with ground glass caps as soon as it was removed from the thermostat. The average mass of at least two fillings which seldom differed by more than 0.0006 g. was taken for calculation. The accuracy of the density measurements, therefore, works to nine parts in a million. Frequent checks were made on the mass and volume of the pyknometer. All the weights were reduced to vacuum standard by using the formula

$$W_v = W + (v_l + v_p - v_w)\rho$$

where ρ is the density of air, W_v weight in vacuum, W weight in air, v_w , v_l and v_p are the volumes of the weights, liquid and pyknometer (weight of pyknometer divided by density of glass), respectively. v_w , v_l and v_p were measured to the second decimal place only. The density of air was measured every day, using the formula $\rho = \frac{W_1 - W_2}{v}$ where W_1 and W_2 are the weights of a sealed flask in vacuum and air respectively and v is its external volume (535.5 c.c.). v was found by weighing the flask in air and

¹ Masson, *Phil. Mag.*, 1929 (7), 8, 218; Geffcken, *Naturwiss.*, 1931, 15, 321.

² Redlich and Rosenfeld, *Z. physik. Chem.*, 1931, 155, 65.

³ Scott and Wilson, *J. Physic. Chem.*, 1934, 38, 951; Frang, *Ann. Physik*, 1938, 31, 681.

⁴ A good bibliography of the work is given in these two papers.

⁵ Srinivasan and Prasad, *Trans. Faraday Soc.*, 1938, 34, 1139.

TABLE I.

Concn.	Density.	ϕ .	P.E.	Concn.	Density.	ϕ .	P.E.
--------	----------	----------	------	--------	----------	----------	------

A. Jones and Ray⁵ (accuracy 6 in a million).Potassium chloride at 25° C. ($\phi = 26.67 + 2.2\sqrt{\phi}$).

0	0.997074			0.02	0.998018	27.44	0.3
0.0001	0.997078	34.66	60	0.05	0.999440	27.31	0.12
0.0002	0.997081	39.67	30	0.1	1.001787	27.51	
0.0005	0.997094	34.65	12	0.2	1.006456	27.73	
0.001	0.997117	31.65	6	0.5	1.020275	28.24	
0.002	0.997161	31.15	3	0.9996	1.042865	28.85	
0.005	0.997306	28.24	1.2	1.9908	1.086749	29.78	
0.01	0.997540	28.04	0.6	2.99647	1.129252	30.53	

Caesium nitrate at 25° C. ($\phi = 51.61 - 0.26\sqrt{\phi}$).

0.0001	0.997088	55.09	60	0.005	0.997791	51.69	1.2
0.0002	0.997101	60.10	30	0.01	0.998509	51.58	0.6
0.0005	0.997138	67.13	12	0.02	0.999944	51.59	0.3
0.001	0.997212	57.10	6	0.05	1.004258	51.40	0.12
0.002	0.997361	51.60	3	0.10001	1.011430	51.53	0.1

B. Present measurements (accuracy 9 in a million).

Potassium nitrate at 35° C. ($\phi = 40.80 + 0.96\sqrt{\phi}$).

0	0.994058			0.020000	0.995190	44.75	0.45
0.001000	0.994092	67.49	9.0	0.040000	0.996510	40.02	0.23
0.002000	0.994128	66.48	4.5	0.060000	0.997665	41.22	0.15
0.004000	0.994241	55.67	2.3	0.080000	0.998893	40.89	0.11
0.006000	0.994335	55.25	1.5	0.30000	1.012064	41.31	0.03
0.008000	0.994490	47.37	1.1	0.59520	1.029703	41.45	0.02
0.010000	0.994635	43.64	0.9	1.00960	1.054206	41.76	0.01

Sodium nitrate at 35° C. ($\phi = 30.30 + 1.27\sqrt{\phi}$).

0.002000	0.994148	40.24	4.5	0.040000	0.996262	30.09	0.23
0.004000	0.994256	35.71	2.3	0.060000	0.997313	30.93	0.15
0.006000	0.994335	39.06	1.5	0.080000	0.998401	30.89	0.11
0.008000	0.994469	33.83	1.1	0.15001	1.002195	30.95	0.06
0.010000	0.994583	32.69	0.9	0.50000	1.021175	30.95	0.02
0.020000	0.995135	31.34	0.45	0.98097	1.046604	31.62	0.01

Potassium chloride at 35° C. ($\phi = 28.40 + 1.5\sqrt{\phi}$).

0.0017325	0.994108	45.99	5.2	0.034650	0.995610	29.94	0.26
0.0034614	0.994157	46.23	2.6	0.052020	0.996413	29.66	0.17
0.0052020	0.994255	36.90	1.7	0.086584	0.998003	29.16	0.10
0.0069228	0.994332	35.18	1.3	0.27207	1.006499	28.99	0.03
0.0086626	0.994410	34.13	1.04	0.54414	1.018704	29.43	0.02
0.017325	0.994839	29.65	0.52	1.0387	1.040503	30.02	0.01

Sodium chloride at 35° C. ($\phi = 18.10 + 1.24\sqrt{\phi}$).

0.002006	0.994113	31.22	4.5	0.060018	0.996442	18.84	0.15
0.0040120	0.994194	24.70	2.3	0.080240	0.997271	18.52	0.11
0.0060180	0.994271	23.20	1.5	0.10030	0.998070	18.56	0.09
0.0080014	0.994355	21.46	1.1	0.30090	1.006072	18.63	0.03
0.010007	0.994429	21.50	0.9	0.58871	1.017433	18.86	0.01
0.019816	0.994825	19.86	0.45	1.0568	1.035453	19.39	0.00
0.039632	0.995640	18.64	0.23				

⁵ Jones and Ray, *J. Amer. Chem. Soc.*, 1937, **59**, 187.

in water without applying any buoyancy correction. In order to know W_1 , one direct determination of the density of air was made.

Merck's "pro analysi" samples of potassium nitrate and sodium nitrate were twice crystallised from double distilled water, dried at 125° C. in an air oven and kept in a vacuum desiccator for use. Samples of sodium

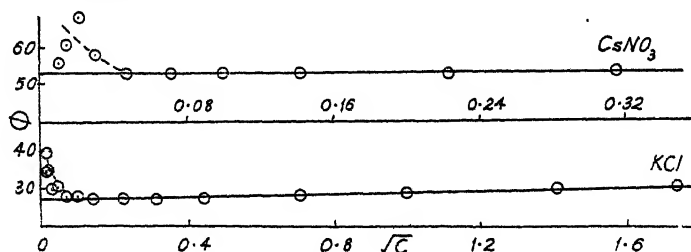


FIG. 1.

chloride and potassium chloride were Kahlbaum's "pro analysi" quality but they were not further crystallised as the analysis given on the bottles showed that they were of a very high order of purity. These samples also were dried in an air oven at 125° C. before use.

A stock solution of the substance of convenient strength was first prepared by weighing out the salt and making up to a definite volume. Calculated volumes of this were measured out from a burette and diluted to 250 c.c. at the temperature of the thermostat. Throughout the work the same measuring vessels were used.

The apparent molal volume was calculated from the equation

$$\phi = \frac{M}{\rho_0} - \frac{(\rho - \rho_0)10^3}{\rho_0 c},$$

where M is the molecular weight, c is the concentration in moles per litre, ρ_0 and ρ density of water and solution respectively. The preceding tables show concentration c , density in gram per c.c., apparent molal volume ϕ in c.c., and the possible error (P.E.) in the value of ϕ , calculated on the basis of the experimental error in the measurement of density, indicated in parenthesis against the name of the experimenters.

Fig. 1 shows the plot of ϕ as calculated from the density data of Jones and Ray² against \sqrt{c} for potassium chloride and caesium nitrate.

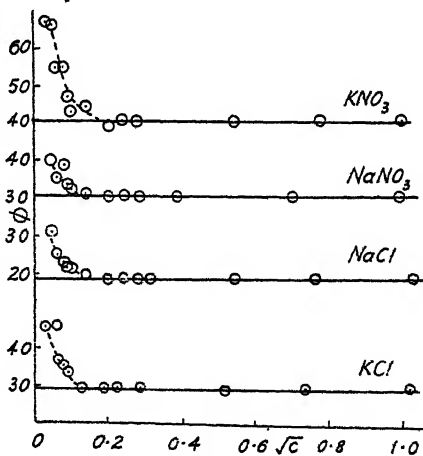


FIG. 2.

Fig. 2 shows the plot of ϕ against \sqrt{c} for NaNO_3 , KNO_3 , NaCl and KCl .

Discussion.

Prang³ has measured the density of sodium chloride and potassium chloride solutions at 18° C. For some sets of values he claims an accuracy of five in the eighth decimal place. Even with these experiments the values of K for KCl (1.73) and NaCl (1.06) are not identical.

Jones and Ray⁵ have measured the density of potassium chloride and caesium nitrate solutions at 25° C. to an accuracy of six parts in a million in connection with their surface tension measurements. Fig. 1 shows the plot of ϕ against \sqrt{c} calculated from these results. As it would not be fair to draw a straight line by the method of least squares on account of the probable error in the values of ϕ at lower concentrations being much greater than at higher concentrations, the points corresponding to very low concentrations have been ignored in drawing the figure. The deviation of these points from the straight line is within experimental error. Here also the values of K for these two salts are different: $K_{\text{KCl}} = 2.20$, $K_{\text{CsNO}_3} = -0.26$. The value of K for CsI calculated from the density data of Jones and Fornwalt⁶ is 1.6.

Our measurements of density for solutions of potassium nitrate, sodium nitrate, potassium chloride and sodium chloride at 35° C. are accurate to nine parts in a million. For reasons stated in the above paragraph we have ignored the points corresponding to very low concentrations in drawing Fig. 2. The values of K after ignoring these points are 0.96, 1.27, 1.5 and 1.24, for KNO_3 , NaNO_3 , KCl and NaCl respectively. However the deviations of many of the points from the straight line (Fig. 2) are not within experimental error. Whether they constitute an actual discrepancy or not, is not possible to say without doing further work.

Taking all these experiments into consideration it could be safely concluded that the value of K for all electrolytes of the mono-monovalent type at least is generally of the same order at the same temperature.

One of us (M. K. S.) is grateful to the Government of Orissa for a research scholarship.

Summary.

The apparent molal volume of some mono-monovalent electrolytes has been studied from the standpoint of the Masson-Redlich-Rosenfeld Law: $\phi = \phi_0 + K\sqrt{c}$. It is found that the values of K are generally of the same order (though not the same) for all electrolytes at the same temperature, except in the case of caesium nitrate at 25° C. where it surprisingly assumes a negative value. The following are the values of K : $K_{\text{KCl}}^{18} = 1.73$, $K_{\text{NaCl}}^{18} = 1.06$; $K_{\text{KCl}}^{25} = 2.20$, $K_{\text{CsNO}_3}^{25} = -0.26$, $K_{\text{CsI}}^{25} = 1.6$; $K_{\text{KNO}_3}^{35} = 0.96$, $K_{\text{NaNO}_3}^{35} = 1.27$, $K_{\text{KCl}}^{35} = 1.5$, $K_{\text{NaCl}}^{35} = 1.24$.

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⁶ Jones and Fornwalt, *J. Amer. Chem. Soc.*, 1936, **58**, 619.

VISCOSITY AND DENSITY OF AQUEOUS SOLUTIONS OF BARIUM CHLORIDE, MAGNESIUM CHLORIDE, COBALT CHLORIDE AND NICKEL CHLORIDE AT 35° C.

BY A. S. CHACRAVARTI AND B. PRASAD.

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Quite a good deal of work has been done both on the viscosity of solutions of electrolytes and their densities at 25° C. However, most of the workers have confined themselves to uni-univalent electrolytes. Jones and Dole¹ have worked on the viscosity of barium chloride solutions at 25° C. It was this work which led to the enunciation of their formula: $\eta/\eta_0 = 1 + A\sqrt{c} + Bc$. Ranade and Paranjpe² have also measured the viscosity of barium chloride solutions at a number of temperatures of which 35.1° C. is one. From the description of their experiments and technique, it is evident that their accuracy is not as high as ours. The discrepancy between their results and ours can be accounted for if we make allowance for their comparatively larger experimental error. Moreover, our work extends both to higher and lower concentration ranges. Dolian and Briscoe³ have measured the viscosity of nickel chloride solutions at 25° C., but their work does not seem to be very accurate and is meagre. Accurate work on the density of solutions of bi-univalent electrolytes is meagre even at 25° C. Geffcken⁴ has used data by Shibata for calculating the apparent molal volumes of barium chloride in aqueous solutions at 25°, 35° and 45° C. but his solutions are more concentrated than ours. Fair comparisons between our results is not possible. In the present investigation, our original idea was to confine ourselves to the testing of the Jones and Dole equation and seeing how far the experimental values of A agreed with the theoretical ones.⁵ So, we used smaller pycnometers (about 20 c.c.) for the determination of the viscosity of barium chloride and magnesium chloride solutions. Later on, we thought it would be worth while to study the variation of the apparent molal volume (ϕ) also in the light of the Masson⁶-Redlich and Rosenfeld⁷ law: $\phi = \phi_0 + K\sqrt{c}$. In the cases of cobalt and nickel chlorides, larger pycnometers (about 60 c.c.) were used for measuring the density of solutions in connection with viscosity work, so as to ensure accuracy of density to the sixth place of decimal. With these density data, the apparent molal volume of cobalt and nickel chloride solutions were determined. The density of barium and magnesium chloride solutions were re-determined with a 60 c.c. pycnometer for the apparent molal volume work.

¹ Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.

² Ranade and Paranjpe, *J. Univ. Bombay*, 1938, **7**, (3), 2.

³ Dolian and Briscoe, *J. Physic. Chem.*, 1937, **41**, 1129.

⁴ Geffcken, *Z. physik. Chem.*, 1931, **155**, 1.

⁵ Falkenhagen and Vernon, *Phil. Mag.*, 1932, **14**, 537.

⁶ Masson, *ibid.*, 1929, (7), **8**, 218.

⁷ Redlich and Rosenfeld, *Z. physik. Chem.*, 1931, **155**, 65.

Experimental.

Merck's reagent quality magnesium chloride, Merck's pro-analysis barium chloride, Scherring Kahlbaum's purest nickel free cobalt chloride and Merck's purest cobalt free nickel chloride were used in the experiments.

The experimental procedure is the same as that given in a previous paper,⁸ except that a telescope giving a linear magnification of three at a distance of 2 feet was used for setting the level of the liquid in the wider limb. The thermostat was maintained at $35^\circ \pm 0.005$. Double distilled

TABLE I.

Concn.	η/η_0 (obs.).	η/η_0 (calc.).	ρ (g./c.c.).	ϕ (c.c.).
Cobalt Chloride, $\eta/\eta_0 = 1 + 0.016\sqrt{c} + 0.370c$; $\phi = 16.0 + 4.2\sqrt{c}$.				
0	I	I	0.994058	—
0.0010	I.0010	I.0009	0.994172	15.97
0.0020	I.0013	I.0014	0.994302	7.93
0.0030	I.0021	I.0020	0.994381	22.34
0.0040	I.0021	I.0025	0.994511	16.72
0.0050	I.0030	I.0030	0.994621	17.37
0.0100	I.0053	I.0053	0.995197	16.06
0.0150	I.0076	I.0076	0.995767	15.52
0.0200	I.0094	I.0097	0.996327	16.52
0.0250	I.0122	I.0118	0.996894	16.54
0.0300	I.0138	I.0139	0.997482	15.84
0.0400	I.0177	I.0180	0.998565	17.30
0.0500	I.0219	I.0221	0.999718	16.77
0.0750	I.0328	I.0322	I.002541	16.87
0.1000	I.0438	I.0421	I.005343	17.13
0.1250	I.0529	I.0520	I.008162	17.15
0.1500	I.0641	I.0617	I.011060	16.63
0.2000	I.0828	I.0812	I.016475	17.86
0.2500	I.1026	I.1005	I.021964	18.33
Nickel Chloride, $\eta/\eta_0 = 1 + 0.028\sqrt{c} + 0.316c$; $\phi = 10.0 + 9.6\sqrt{c}$.				
0.0010	I.0008	I.0012	0.994146	41.87
0.0020	I.0021	I.0019	0.994264	26.78
0.0030	I.0027	I.0024	0.994404	14.37
0.0040	I.0033	I.0031	0.994506	17.72
0.0050	I.0037	I.0036	0.994614	18.53
0.0100	I.0062	I.0060	0.995214	14.12
0.0150	I.0083	I.0081	0.995813	12.70
0.0200	I.0100	I.0103	0.996408	12.19
0.0250	I.0121	I.0123	0.997078	8.87
0.0300	I.0146	I.0144	0.997724	7.47
0.0400	I.0178	I.0182	0.998794	11.31
0.0500	I.0226	I.0221	0.999960	11.65
0.0750	I.0327	I.0314	I.002851	12.45
0.1000	I.0431	I.0405	I.005715	13.13
0.1250	I.0536	I.0494	I.008601	13.37
0.2000	I.0833	I.0757	I.017147	14.26

water was used for making all the solutions. No kinetic and surface tension correction was deemed necessary with the viscometers. The length of the capillary tube in both the viscometers used was about 10 cm. The diameter of the capillary tube and the approximate time of efflux for water were 0.28 mm. and 29 minutes for one and 0.35 mm. and 15 minutes for the other. The viscometer having a smaller time of efflux was used for concentrated solutions of barium and nickel chlorides. For all other solutions, the other viscometer was used. Five readings for the time of flow, seldom differing

⁸ Srinivasan and Prasad, *Trans. Faraday Soc.*, 1938, **34**, 1139.

from one another by more than 0.2 sec. and two readings for the mass of solution differing from each other by less than 0.001 g. were taken in case of every solution. The error in relative viscosity is not expected to exceed 0.0003 in experiments with the viscometer having a longer time of flow. Both before and after working with a solution, the viscometer was tested with water.

The pyknometers had vertical capillary limbs with marks. They could be immersed in the thermostat up to 3 cm. above the marks. After keeping them in the thermostat for half an hour, the level of the liquid in the limbs was adjusted to these marks with a fine platinum syringe. To avoid evaporation, the capillary limbs were fitted with well ground glass caps. The pyknometers used for the density measurements of cobalt and nickel chloride solutions in connection with their viscosity as well as the pyknometers used for barium and magnesium chloride solutions in connection

TABLE II.

Concn.	η/η_0 (obs.).	η/η_0 (calc.).	Concn.	η/η_0 (obs.).	η/η_0 (calc.).
Barium Chloride, $\eta/\eta_0 = 1 + 0.018\sqrt{c} + 0.285c$.			Magnesium Chloride, $\eta/\eta_0 = 1 + 0.017\sqrt{c} + 0.370c$.		
0.0015	1.0012	1.0011	0.0025	1.0016	1.0018
0.0020	1.0014	1.0014	0.0040	1.0024	1.0026
0.0025	1.0017	1.0016	0.0050	1.0034	1.0031
0.0030	1.0021	1.0019	0.0150	1.0078	1.0076
0.0035	1.0019	1.0021	0.0300	1.0140	1.0141
0.0040	1.0025	1.0022	0.0450	1.0199	1.0203
0.0045	1.0023	1.0025	0.0600	1.0265	1.0264
0.0050	1.0029	1.0027	0.0750	1.0323	1.0324
0.0100	1.0045	1.0047	0.1000	1.0422	1.0424
0.0150	1.0061	1.0065	0.1250	1.0522	1.0523
0.0200	1.0085	1.0082	0.1500	1.0620	1.0621
0.0250	1.0100	1.0099	0.1750	1.0725	1.0718
0.0300	1.0117	1.0117	0.2000	1.0827	1.0816
0.0350	1.0138	1.0134	0.2250	1.0921	1.0913
0.0400	1.0146	1.0150	0.2500	1.1023	1.1010
0.0450	1.0161	1.0166	0.3000	1.1225	1.1203
0.0500	1.0180	1.0183	0.4000	1.1651	1.1588
0.1000	1.0307	1.0342			
0.2000	1.0577	1.0650			
0.3000	1.0863	1.0954			
0.4000	1.1140	1.1254			

with their apparent molal volumes had capacities of about 57 and 64 c.c. The one used for the viscosity determinations of the latter two substances had a volume of about 19 c.c.

For apparent molal volume calculations, all weights were reduced to vacuum, as described in a previous communication.* The error in density measurements is not likely to exceed sixteen in a million in any case, but in most cases the error is much less.

Apparent molal volume (ϕ) was calculated from the equation

$$\phi = \frac{M}{\rho_0} - \frac{10^3(\rho - \rho_0)}{\rho_0 c},$$

where M is the molecular weight of the solute, ρ and ρ_0 the density of solution and solvent respectively and c the concentration of the solute in gram moles per litre.

In all cases, a stock solution was prepared whose strength was carefully determined volumetrically. The solution was diluted and a known volume

* Srinivasan and Prasad, *Trans. Faraday Soc.* (This vol., p. 1462.)

of the dilute solution was treated with sodium carbonate solution to precipitate the heavy metal. The heavy metal carbonate was filtered off and the filtrate, after being acidified with nitric acid was titrated with silver nitrate by Volhard's method as modified by Rothmund and Burgstaller.¹⁰ Some of these results were also confirmed gravimetrically. In order to prepare a solution of any concentration, a definite volume either of the stock solution or of a solution prepared by diluting the stock solution was diluted to 250 c.c. at 35° C. The error in concentration measurement is expected to be much less than 1 per cent.

TABLE III.

Conc. $\times 10^4$.	ρ (g./c.c.).	ϕ (c.c.).	Conc. $\times 10^4$.	ρ (g./c.c.).	ϕ (c.c.).
Barium Chloride, $\phi = 28.2 + 5.5\sqrt{c}$.			Magnesium Chloride, $\phi = 15.0 + 6.0\sqrt{c}$.		
11.77	0.994255	41.16	20.00	0.994217	15.26
23.54	0.994469	33.91	40.00	0.994357	20.04
35.31	0.994690	29.48	60.00	0.994517	18.24
58.85	0.995118	28.35	80.00	0.994678	17.28
235.4	0.998263	29.85	201.0	0.995608	17.68
412.0	1.001472	28.52	503.0	0.998017	16.06
588.5	1.004627	28.91	1006	1.001887	16.94
2354	1.035858	30.91	3018	1.017123	18.36
4120	1.066883	31.74	5030	1.031930	19.50
5885	1.097480	32.76			
7651	1.128150	33.24			

In Tables I, II and III, concentration in gram moles per litre, relative viscosity ($\eta^{35^\circ}/\eta_0^{35^\circ}$) both observed and calculated from the Jones and Dole equation, density ρ and apparent molal volume ϕ are given for the various substances.

In the following figure, apparent molal volume ϕ is plotted against the square root of concentration for the various substances.

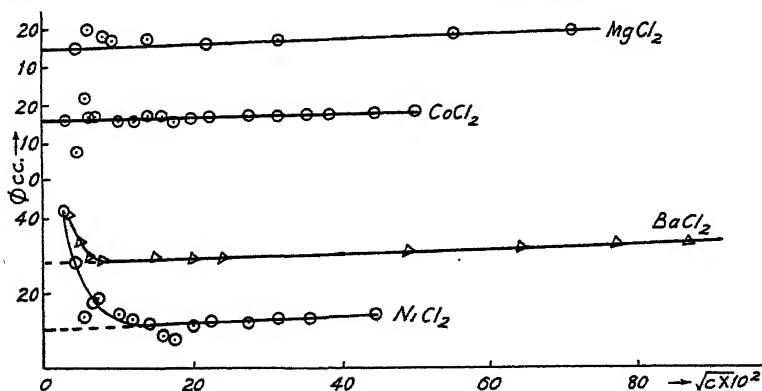


FIG. 1.

Discussion.

The values of A and B for the various electrolytes were obtained by plotting $(\eta/\eta_0 - 1)/\sqrt{c}$ against \sqrt{c} for the dilute range, the slope giving

¹⁰ Rothmund and Burgstaller, *Z. anorg. Chem.*, 1909, **63**, 330; *Analytical Chemistry*, Treadwell and Hall, Vol. II, p. 604 (1930).

B and the ordinate A . The values of A for BaCl_2 and MgCl_2 could be accurately calculated from Falkenhagen and Vernon equation because the mobilities of Ba^{++} and Mg^{++} and their variation with temperature are known. In the cases of CoCl_2 and NiCl_2 , the values of the mobilities of Co^{++} and Ni^{++} are known only at 18°C . and their variation with temperature is not known. The A values for CoCl_2 and NiCl_2 were calculated by assuming that the temperature coefficient of mobility for Co^{++} and Ni^{++} is the same as that for other divalent ions having the same mobility as Co^{++} or Ni^{++} at 18°C .

The calculated and experimental values of A are as follows :—

	BaCl_2	MgCl_2	CoCl_2	NiCl_2
Experimental	0.018	0.017	0.016	0.028
Calculated	0.015	0.017	0.018	0.018

The agreement between the observed and calculated values of BaCl_2 , MgCl_2 and CoCl_2 is good but in the case of NiCl_2 it is not so.

The tables show that the observed values of viscosity and those calculated from the Jones and Dole equation generally do not differ by more than the possible experimental error in the dilute range. Beyond a certain concentration, this difference far exceeds the experimental error. The limit up to which the equation holds good in case of any electrolyte is indicated by the calculated values printed in bold types. It is seen that the limit of applicability is different in each case.

As is evident from the figure, ϕ plotted against \sqrt{c} gives a straight line for concentrations greater than 0.025 moles per litre in every case. For BaCl_2 , MgCl_2 and CoCl_2 , the deviations from the straight line of points corresponding to lower concentrations are within experimental error. Only in the case of NiCl_2 , where the maximum experimental error for the lowest concentration is 16, some of the points lie beyond the possible experimental error. However, it is noteworthy that most of the deviations at low concentrations are on the positive side. There is no doubt that all the deviations at low concentrations are not due to experimental error. According to the theory of Redlich and Rösenfeld, the value of K in the equation $\phi = \phi_0 + K\sqrt{c}$ should be the same for all electrolytes of the same valence type. This is not borne out by our experiments even if K is calculated from the straight line covering points corresponding to higher concentrations.

	BaCl_2	MgCl_2	CoCl_2	NiCl_2
K	5.5	6.0	4.2	9.6

Nickel chloride is marked out both as regards viscosity and apparent molal volume. The A value of NiCl_2 is 0.028 as against 0.018, the calculated value. The value of K also is higher than in all other cases.

One of us (A. S. C.) is grateful to the Government of Orissa for the grant of a research scholarship. We thank Mr. H. Behera for making the necessary viscometers and pycnometers.

Summary.

1. Viscosity of barium chloride, magnesium chloride, cobalt chloride and nickel chloride solutions and apparent molal volume of these electrolytes in aqueous solutions have been measured.

2. Viscosity of all the solutions obeys Jones and Dole equation. The calculated values of A (0.015, 0.017, 0.018) for barium chloride, magnesium chloride and cobalt chloride agree with the experimental values (0.018, 0.017, 0.016). In the case of nickel chloride, the divergence is quite appreciable; calculated 0.018, experimental 0.028.

3. The apparent molal volumes are found to be linear functions of \sqrt{c} , at least for concentrations greater than 0.025 moles/litre. For lower concentrations, some of the deviations seem to be real.

4. The value of K in the equation $\phi = \phi_0 + K\sqrt{c}$ should be the same for all the electrolytes used but it is not so.

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ELECTRON ENERGY LEVELS IN NaCl.

By S. R. TIBBS.

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Many experiments have been carried out on the absorption bands in polar crystals; both on the normal ultra-violet absorption of the pure crystals¹ and also on the absorption in the visible region of the spectrum which occurs in crystals containing colour-centres.² It has been suggested³ that these colour-centres, or F-centres, in alkali-halide crystals are electrons trapped in holes formed by the removal of negative ions. Theoretical information regarding the energies of the conduction levels of a polar crystal and of the energy levels of an electron trapped at a vacant, negative-ion, lattice point is therefore of some importance. In Part I of this paper we calculate the breadth of the first band of allowed conduction levels for the (100) direction in sodium chloride. Comparison of this breadth with the corresponding results for free electrons shows that the conduction electrons have an effective mass of the order of magnitude of that of a free electron. The second part of the paper describes attempts to ascribe to an electron at a vacant, negative-ion, lattice point wave functions which give rise to energy levels which are in agreement with the experimental data on F-centres.

Part 1.

Calculations on the energies of the conduction electrons in a metal, which take account of the crystal structure of the metal, were made possible by a method due to Wigner and Seitz.⁴ They showed how to calculate the energy of the lowest conduction level in the crystal and from these calculations it is possible to derive the lattice spacing and elastic constants of the metal. It was shown by Fuchs,⁵ for copper,

¹ E. G. Schneider and H. M. O'Bryan, *Phys. Rev.*, 1937, **51**, 293; Hilsch and Pohl, *Z. Physik*, 1930, **59**, 812.

² Pohl, *Proc. Phys. Soc.*, 1937, **49**, extra part, 3.

³ de Boer, *Rec. Trav. chim. Pays-Bas*, 1937, **56**, 301.

⁴ Wigner and Seitz, *Phys. Rev.*, 1933, **43**, 804; Wigner, *Phys. Rev.*, 1934, **46**, 1002.

⁵ K. Fuchs, *Proc. Roy. Soc.*, 1935, **151**, 585.

that when the exchange between the conduction electrons and the positive ion cores is taken into account this method gives results which are in good agreement with experiment. The method was later extended by Slater⁶ to give the energies of the higher conduction levels, and so to give the widths of the allowed energy bands for any given direction of motion in the crystal. The energy values given by this method for the higher bands cannot, however, be relied upon to more than a factor of a half,⁷ and it seems that an alternative method, also due to Slater,⁸ will give better numerical results. Owing to its relative simplicity we have been content, in this paper, to use Slater's extension of the Wigner-Seitz method, and have applied it to obtain the energies and wave functions of conduction electrons in a sodium chloride crystal.

It is important to make quite clear what we mean by a conduction electron in a polar crystal which is normally an insulator. A sodium chloride crystal is made up of the ions Na^+ and Cl^- , both of which have

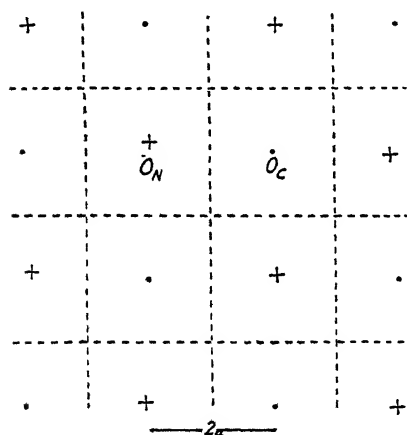


FIG. 1.— Na^+ , Cl^- .

complete electronic shells. In the field due to these ions we will have bands of energy levels, normally empty, which run through the crystal. An extra electron introduced into one of these levels will not be confined to any particular ion but will be free to move through the crystal. We term such an electron a conduction electron and the corresponding levels are referred to as the conduction levels of the crystal.

Slater's extension of the Wigner-Seitz method has already been used by Shockley⁹ in discussing the full energy bands of the crystal. Owing to the lattice structure, the energy levels of the electrons in the outer

shells of the ions are broadened into bands. It is this broadening of the $3p$ level of Cl^- , and the breadths of the bands of allowed energies of an excited $3p$ electron, which have been investigated by Shockley. He finds that the $3p$ band of Cl^- has a width of ~ 4.5 eV., whereas observations due to Skinner¹⁰ of the chlorine K emission bands lead us to expect a much smaller value. In his calculations Shockley has treated each $3p$ electron as moving in an electrostatic field, but for an electron in a full band the interaction with the other electrons is not equivalent to an electrostatic field. Also, no attempt has been made to obtain a self-consistent solution. Ewing and Seitz¹¹ have found a self-consistent field for the $2p$ electrons of F in LiF and deduce a band width (~ 2.3 eV.) which is in good agreement with experiment. Moreover, it is very difficult to correlate the breadth of the Cl^-3p band with the ultraviolet absorption of the crystal, as the absorption spectrum may be regarded as a series of absorption lines, broadened by lattice vibrations,

⁶ J. C. Slater, *Physic. Rev.*, 1934, 45, 794.

⁷ W. Shockley, *ibid.*, 1937, 51, 379.

⁸ W. Shockley, *ibid.*, 1936, 50, 754.

⁹ H. W. B. Skinner, to be published.

¹¹ D. H. Ewing and F. Seitz, *Physic. Rev.*, 1936, 50, 760.

⁸ J. C. Slater, *ibid.*, 846.

leading up to a series limit corresponding to the excitation of a $3p$ electron into the conduction band.¹² It is on account of this view of the absorption process that we have carried out these calculations on the energies of the conduction levels.

The crystal structure of sodium chloride is simple cubic, alternate lattice positions being occupied by Na^+ and Cl^- ions respectively (Fig. 1). If we draw the planes bisecting at right angles the lines joining any ion to its six nearest neighbours, we surround each ion by a cube. These cubes just fill the space occupied by the crystal and have been termed by Wigner and Seitz the atomic cells.

The field in which the conduction electron moves will be periodic with the period of the lattice. Using natural atomic units, the wave equation to be satisfied by the wave function ψ of the electron is

$$\nabla^2 \psi + 2(E - V)\psi = 0, \quad (1)$$

where V is the potential energy of the electron and is a periodic function with the period of the lattice. It has been shown by Bloch that the solution of (1) must be of the form

$$\psi_k(x, y, z) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(x, y, z), \quad (2)$$

where u_k is a function having the period of the lattice and depending, in general, on \mathbf{k} . If we consider a given direction in the crystal it is found that for some values of the energy E the vector \mathbf{k} becomes imaginary. The wave function (2) is then no longer bounded and so cannot represent an electron in the crystal. Thus for a given direction of motion of the electron we have bands of allowed and disallowed energies, and if we draw the curves which give the energy as a function of k we get curves like those shown in Fig. 2.

The energy gaps ΔE separating the bands of allowed energies, occur, in a simple cubic structure of lattice constant a , for values of \mathbf{k} such that

$$k_x n_1 + k_y n_2 + k_z n_3 = \pi(n_1^2 + n_2^2 + n_3^2)/a, \quad (3)$$

where n_1 , n_2 and n_3 are the Miller indices of the planes at which Bragg reflexion takes place.

For a lattice of atoms of the same type, in which each atom may be treated as a centre of symmetry, it can be shown that the wave function must be of the form

$$\psi_k(\mathbf{r}) = \sum_{\alpha} e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}} \phi(\mathbf{r} - \mathbf{R}_{\alpha}), \quad (4)$$

where \mathbf{R}_{α} is the position vector of any centre of symmetry. $\phi(\mathbf{r} - \mathbf{R}_{\alpha})$

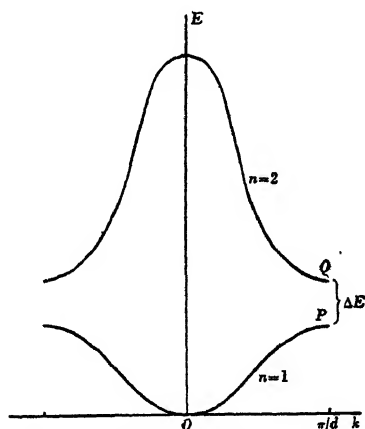


FIG. 2.—Curves showing the energy E as a function of k for a given direction in the crystal; d is the distance between the corresponding planes for which Bragg reflexion takes place.

¹² Peierls, *Ann. Physik*, 1932, 13, 905.

may then be expanded in terms of spherical harmonics and the corresponding radial functions s , p , d , . . . which are the solutions of

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \cdot \frac{dR}{dr} + \left[2E - 2V - \frac{l(l+1)}{r^2} \right] R = 0, \quad (5)$$

for $l = 0, 1, 2, \dots$ V is the potential energy of an electron in the neighbourhood of a centre of symmetry. For a lattice of two types of atoms, *e.g.* sodium chloride, in which each atom can be treated as a centre of symmetry, the wave function must then be of the form

$$\psi_k(\mathbf{r}) = \sum_N e^{i\mathbf{k} \cdot \mathbf{R}_N} \phi_N(\mathbf{r} - \mathbf{R}_N) + \sum_C e^{i\mathbf{k} \cdot \mathbf{R}_C} \phi_C(\mathbf{r} - \mathbf{R}_C) \quad (6)$$

where the suffixes N and C refer to the sodium and chlorine ions respectively.

Now the wave function, together with its first derivative, must be continuous everywhere. Therefore these conditions must be satisfied at all points on the boundary planes of the atomic cells. Actually, it is not practicable to satisfy these boundary conditions rigorously at all points of the boundary. Following Slater, we replace them by simpler and more practicable boundary conditions. We choose the boundary conditions to be that the wave function, with its derivative normal to the boundary plane, must be continuous at the midpoints of the six faces of the atomic cells.

We now write

$$\begin{aligned} \phi_N &= u_N + iv_N \\ \phi_C &= u_C + iv_C \end{aligned} \quad (7)$$

where u_N , u_C and v_N , v_C are (a) real, (b) even and odd respectively with respect to inversions in their respective origins, *i.e.* u_N , u_C contain spherical harmonics of even order and v_N , v_C those of odd order. Let $2a$ be the distance between two adjacent ions, so that the lattice constant is $4a$. Taking the origin at a sodium ion, the six neighbouring chlorine ions are at the lattice points $\pm(2a, 0, 0)$, $\pm(0, 2a, 0)$ and $\pm(0, 0, 2a)$. The continuity of the wave function at the midpoint $(a, 0, 0)$ gives

$$(u_N + iv_N)_{(a, 0, 0)} = e^{i2k_x a} (u_C + iv_C)_{(-a, 0, 0)} = e^{i2k_x a} (u_C - iv_C)_{(a, 0, 0)}.$$

The condition for the continuity of the normal derivative at the point $(a, 0, 0)$ is

$$(u'_N + iv'_N)_{(a, 0, 0)} = -e^{i2k_x a} (u'_C - iv'_C)_{(a, 0, 0)}$$

where the accent denotes $\partial/\partial r$. With functions of the type used the boundary conditions for the point $(-a, 0, 0)$ give rise to conditions equivalent to those for $(a, 0, 0)$. Similarly the boundary conditions for midpoints $(0, \pm a, 0)$ and $(0, 0, \pm a)$ give

$$\begin{aligned} (u_N + iv_N)_{(0, a, 0)} &= e^{i2k_y a} (u_C - iv_C)_{(0, a, 0)} \\ (u'_N + iv'_N)_{(0, a, 0)} &= -e^{i2k_y a} (u'_C - iv'_C)_{(0, a, 0)} \\ (u_N + iv_N)_{(0, 0, a)} &= e^{i2k_z a} (u_C - iv_C)_{(0, 0, a)} \\ (u'_N + iv'_N)_{(0, 0, a)} &= -e^{i2k_z a} (u'_C - iv'_C)_{(0, 0, a)}. \end{aligned}$$

In order to be able to satisfy these six equations we must have twelve arbitrary constants at our disposal. We therefore write

$$\begin{aligned}
u_N &= As_N + [B(x^2 - y^2) + C(y^2 - z^2)]d_N/r^2, \\
v_N &= (lx + my + nz)p_N/r, \\
u_O &= \alpha s_O + [\beta(x^2 - y^2) + \gamma(y^2 - z^2)]d_O/r^2, \\
v_O &= (\lambda x + \mu y + \nu z)p_O/r. \quad (8)
\end{aligned}$$

We have not thought it necessary, with our particular problem in mind, to try and obtain a general solution of these equations, nor to try and obtain a general relation connecting E and k for the particular direction in which we are interested. For all we require is the energy values corresponding to the bottom and top of the first band of allowed levels and to the bottom of the second band for motion in the (100) direction, *i.e.* we require the energies corresponding to the states O, P and Q of Fig. 2. The corresponding values of \mathbf{k} are, from (3),

$$k_x = 0, \frac{\pi}{2a}, \text{ and } k_y = k_z = 0.$$

The solutions for these particular values of \mathbf{k} are :

(a) All the coefficients zero except A and α . We must then have

$$\frac{s'_N}{s_N} = -\frac{s'_O}{s_O} \quad (9a)$$

at $r = a$, an equation defining the energy of the level. The wave function contains only s functions, and so this level is referred to as an s -level.

(b) All the coefficients zero except l, m, n, λ, μ and ν . We must have

$$\frac{p_N}{p_N} = -\frac{p'_O}{p_O} \quad (9b)$$

at $r = a$, and this level will be referred to as a p -level.

(c) $B = 2C, \beta = 2\gamma$, and all the other coefficients zero except A and α . This requires

$$8\left(\frac{s'_N}{s_N} + \frac{d'_O}{d_O}\right)\left(\frac{s'_O}{s_O} + \frac{d'_N}{d_N}\right) + \left(\frac{s'_N}{s_N} + \frac{d'_N}{d_N}\right)\left(\frac{s'_O}{s_O} + \frac{d'_O}{d_O}\right) = 0 \quad (9c)$$

at $r = a$.

The wave function is a combination of s and d functions, and will be referred to as the (s, d) level. The condition (9a) defines the energy of the lowest conduction level in the crystal; of (9b) and (9c) the one having the lower energy will be the top of the first band (corresponding to the state P, Fig. 2) and the one of higher energy will presumably be the bottom of the second band.

We have tacitly assumed in the preceding discussion that the potential energies V_N and V_O , of an electron within the atomic cells of a sodium and chlorine ion respectively, are spherically symmetrical about their respective origins O_N and O_O . For the real crystal this is not true; the field along the line joining a Na^+ ion to a neighbouring Cl^- ion is not the same as the field along the line joining two neighbouring Na^+ ions or two neighbouring Cl^- ions. Also, the energy relations (9) depend only on the values of the spherically symmetric functions

$$\left(\frac{s'_N}{s_N}\right), \left(\frac{s'_O}{s_O}\right) \dots \text{ at } r = a.$$

We therefore replace each atomic cell by a sphere of equal volume, taking the potential field inside the sphere to be spherically symmetrical and the same as that along the (100) direction. We shall refer to these spheres as the "ionic spheres." The midpoints of the six boundary planes of an atomic cell are then replaced by the points of contact of any sphere with its six neighbouring spheres. The functions

$$\left(\frac{s'_N}{s_N}\right), \left(\frac{s'_C}{s_C}\right), \dots$$

are then evaluated for $r = R$, where R is the radius of the sphere.

The potential field to be used for the calculation of the radial wave functions s_N, s_C, \dots is rather important. The self-consistent field,

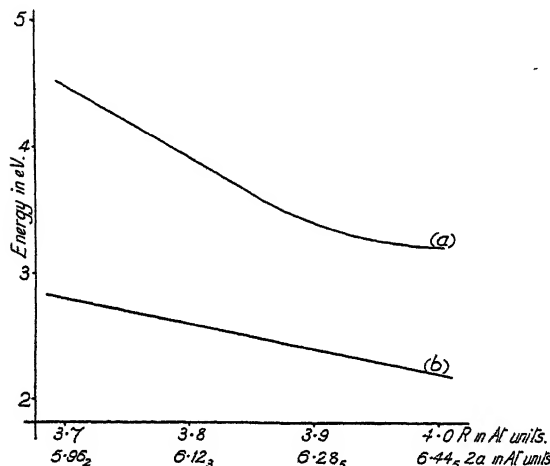


FIG. 3.

without exchange, for the free chlorine ion has been given by Hartree,¹³ and the field of the sodium ion may be taken to be that given by Prokofjew.¹⁴ In the crystal, the potential field at a point near a chlorine ion say, is that due to the chlorine ion plus the potential field at that point due to all the other ions of the crystal. Moreover, the potential field of a chlorine ion in the

crystal will not be quite the same as that given by Hartree, for the outer electrons of the ion will be disturbed by the presence of the other ions of the crystal.

The potential energy of an electron at any lattice point, due to all the other ions, treated as point charges, is $\pm \alpha e^2/2a$, where α is the Madelung constant (1.747 for NaCl) and $2a$ is the distance between nearest neighbours. Midway between two unlike ions the potential energy due to all the other ions is zero, so that the potential energy of an electron at this point is just the sum of those due to these two ions; i.e. it is $V_N(a) + V_C(a)$. We therefore assume that the potential energy of an electron within the ionic sphere of a Na^+ ion, at a distance r from the nucleus, is of the form

$$V_N(r) + \frac{\alpha e^2}{2a} + A_N r^2 + B_N r^3, \quad (10)$$

where A_N and B_N are constants. Similarly, within the ionic sphere of a Cl^- ion we assume the potential energy of the electron to be

$$V_C(r) - \frac{\alpha e^2}{2a} + A_C r^2 + B_C r^3. \quad (11)$$

¹³ D. R. Hartree, *Proc. Roy. Soc.*, 1933, 141, 282.

¹⁴ W. Prokofjew, *Z. Physik*, 1929, 58, 255.

The constants are chosen so that the potential energy has the value $V_N(R) + V_O(R)$ at $r = R$ in each case, and so that the derivative of the potential energy is continuous at this point. We feel that this is the best simple approximation which can be obtained to the actual potential energy along the (100) direction in the crystal.

The potential energy given by (10) and (11) was calculated for several values of the radius R of the ionic spheres. Using these potential energies we have calculated, by the usual method,¹⁵ the radial wave functions s_N , s_O , and so, from the boundary condition (9a) obtained the energy of the lowest conduction level in each case. Curve A of Fig. 3 shows the variation of the energy of the lowest conduction level with R ; curve B shows the variation of $\alpha e^2/2a - I$, where I is the ionisation energy of sodium, which is the energy of an electron placed on a sodium ion in the crystal. The energy of the lowest conduction level has been estimated by Mott¹⁶ to be -0.5 eV., so that our calculations give much too high an energy. The calculations of Mott and Littleton¹⁷ on the polarisation energy of an electron in a polar crystal leads us to expect a decrease in our calculated energy of about two electron volts. The taking into account of exchange effects would also result in a lowering of the calculated energy, but it is not possible to estimate the magnitude of the correction.

We arrived at a value for the "theoretical radius" of the ionic spheres from a consideration of the diamagnetic properties of the chlorine ions. The self-consistent field calculations for Cl^- , without exchange, lead to a value of -41.3×10^{-6} for the diamagnetic susceptibility,¹⁸ whereas the observed value is -25×10^{-6} . Hence, when using the self-consistent field without exchange for Cl^- , the observed radius of the ion should be increased in the ratio $\sqrt{\frac{41.3}{25}}$. This leads to a value

of $R = 4.0$ At. units as a convenient theoretical radius of the ionic spheres. We then assume that the calculated spacing of the allowed bands of conduction levels, for this value of R , will be of the same order of magnitude as for the real crystal.

The radial wave functions p_N , p_O , d_N , d_O were then calculated for the potential energy corresponding to a radius $R = 4.0$ At. units of the ionic spheres, and then the energy conditions (9) were used to obtain the energies of the higher levels. The results are shown diagrammatically in Fig. 4 and the corresponding wave functions, along the (100) direction, for the s and p levels are shown in Fig. 5. From Fig. 4 it will be seen that the breadth of the first band of allowed levels is ~ 5.45 eV. For free electrons the energy, above the lowest level, of an electron with wave vector \mathbf{k} is given by $\frac{\hbar^2 k^2}{2m}$, so that for $k = \frac{\pi}{2a}$ the energy is $\frac{\hbar^2 \pi^2}{8ma^2}$.

¹⁵ D. R. Hartree, *Proc. Camb. Phil. Soc.*, 1928, **24**, 89.

¹⁶ N. F. Mott, *Trans. Faraday Soc.*, 1938, **34**, 500.

¹⁷ Mott and Littleton, *ibid.*, 1938, **34**, 485.

¹⁸ D. R. Hartree, *Proc. Roy. Soc.*, 1936, **156**, 45.

Putting in the value of a for the real crystal this gives an energy of ~ 4.7 eV., so that the effective mass of the conduction electrons is probably ~ 0.87 , which agrees almost too well with the value 0.9 obtained by Frolich¹⁹ from a consideration of the dielectric breakdown in polar crystals.

Part 2.

When an alkali-halide crystal is heated in the vapour of the alkali metal it acquires a deep characteristic colour; e.g. sodium chloride

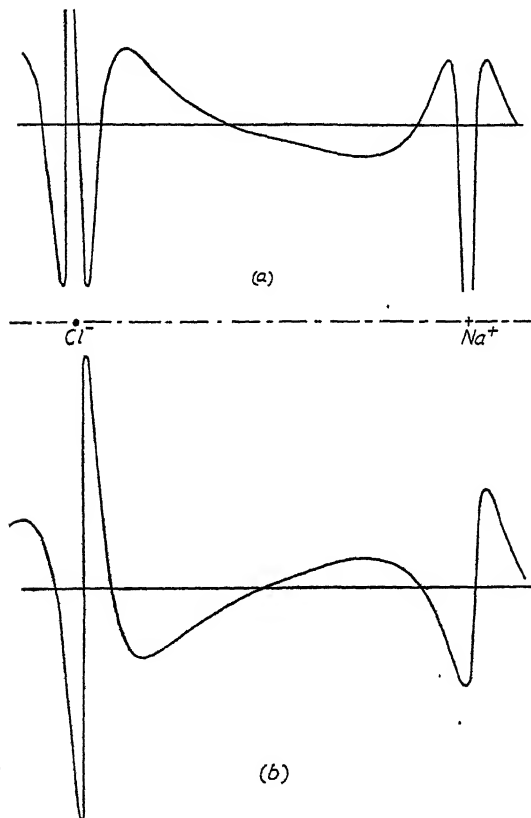


FIG. 5.—Wave functions, along the 100 direction, for a conduction electron in NaCl. (a) s function;

$$k_x = k_y = k_z = 0.$$

(b) p function;

$$k_x = \frac{\pi}{2a}, k_y = k_z = 0.$$

becomes yellow and potassium chloride deep blue. This coloration is due to the presence of a characteristic absorption band, called the F-band, whose maximum lies in, or very near, the visible region of the spectrum. The F-bands for the alkali-halides have been investigated in detail by Pohl and his co-workers.² The presence of these F-bands may be explained as follows: on being heated in the alkali vapour a crystal acquires a stoichiometric excess of metal. This metal may be taken up in one of two possible ways; the crystal may either contain metal atoms in interstitial positions or there may be a number of vacant lattice points from which negative ions are missing. In the latter case,

¹⁹ To be published, *Proc. Roy. Soc.*

in order to keep the crystal electrically neutral, we must add electrons to the crystal. Now an electron, as we shall show in the next paragraph, can be trapped in the potential hole at one of these vacant lattice points, and may occupy any one of a series of possible energy levels. The characteristic absorption band of the crystal containing excess metal may therefore be due to the excitation of electrons trapped in the crystal in this way. An electron trapped at a vacant, negative-ion lattice point will be referred to as an F-centre.

A perfect polar crystal will be electrically neutral. Suppose that a negative ion is removed from the interior of such a crystal, leaving a vacant, negative-ion lattice point. This is equivalent to putting a positive charge at the point in the crystal from which the negative ion is removed. This positive charge gives rise to an electric field and the crystal becomes polarised. If we consider the crystal as being a uniform dielectric medium, the potential field in the crystal due to this positive charge is $e/K \cdot r$, where K is the dielectric constant for static fields; thus K includes the contribution to the polarisation of the medium due to the displacement of the ions from their normal positions in the perfect lattice. The potential energy of an electron in this field will be $-e^2/K \cdot r$, and there will exist a series of possible energy levels for the electron in this potential hole. But if we introduce an electron into the lowest energy state in this potential hole the crystal is again electrically neutral. At large distances from the hole, *i.e.* outside the orbit of the electron, the ions will move back into their normal positions. Hence, in calculating the possible energy levels into which an electron may be excited by the absorption of light, we must take the potential energy of the electron at large distances from the vacant lattice point to be $-e^2/K_0 r$, where K_0 is the dielectric constant for alternating fields of frequency large compared with that of the residual rays ($5 \times 10^{12} \text{ sec}^{-1}$).

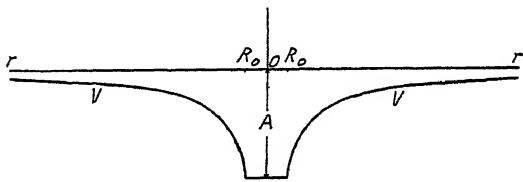


FIG. 6.

The potential energy of the electron at small distances is not so easily determined, but there are two possible ways of fixing the potential energy at the vacant lattice point. We may say that it is the potential energy due to the charges on all the other ions, treated as point charges, in a medium of dielectric constant K_0 . Then the potential energy of an electron placed at the vacant lattice point will be $-ae^2/K_0 \cdot 2a$. Alternatively, we may use the method of Schottky and Jost and treat the crystal as a uniform dielectric with a hole of radius R in it. The potential at the centre due to the polarisation of the medium is then

$$-(1 - 1/K_0)Q/R,$$

where Q is the total effective charge of the medium. Our second estimate for the potential energy of an electron at the vacant lattice point is therefore

$$-ae^2/2a + e^2(1 - 1/K_0)/R.$$

The potential hole due to the missing negative ion is not actually spherically symmetrical, but in order to carry out calculations on the energy levels of an electron trapped in the hole it is necessary to replace

the actual hole by one having spherical symmetry. We choose, as the simplest approximation the potential hole shown in Fig. 6. The constant potential energy $-A$, for $r \leq R_0$, is chosen to be

$$-\alpha e^2/2a + e^2(1 - 1/K_0)/R,$$

and the value of R_0 is then fixed by the condition that $A = e^2/K_0 R_0$, i.e. $R_0 = e^2/K_0 A$. Mott and Littleton¹⁷ have calculated the values of the radius R of the hole in the dielectric for the removal of ions from various crystals. For the removal of a Cl^- ion from NaCl they find that

$$R = 0.95 \times 2a.$$

For NaCl, $K_0 = 2.33$, $\alpha = 1.747$ and $2a = 5.33$ At. units which give $A = 5.82$ eV. and $R_0 = 2.0$ At. units.

The wave function ψ of the electron, using natural atomic units, is a proper solution of

$$\nabla^2 \psi + 2(E - V)\psi = 0,$$

where V is the function plotted in Fig. 6. Writing, in the usual notation,

$$\psi = \frac{1}{r} P(r) S_l(\theta, \phi),$$

$P(r)$ is a solution of

$$\frac{d^2 P}{dr^2} + \left[2E - 2V - \frac{l(l+1)}{r^2} \right] P = 0. \quad (1)$$

For s -states $l = 0$, and so for $r \leq R_0$ the equation (1) becomes

$$\frac{d^2 P}{dr^2} + \omega^2 P = 0 \quad (2)$$

where $\omega^2 = 2(E + A)$, giving

$$P = B \sin \omega r + C \cos \omega r.$$

But ψ must be finite at $r = 0$, $\therefore C = 0$. Hence for the s -states

$$\psi = B \frac{\sin \omega r}{r} \quad \text{for } r \leq R_0. \quad (3)$$

For $l = 0$ and $r > R_0$ equation (1) becomes

$$\frac{d^2 P}{dr^2} + \left[2E + \frac{2}{K_0 r} \right] P = 0. \quad (4)$$

This equation is solved numerically for various energies E by integrating inwards from $r = \infty$ up to $r = R_0$. Denoting the solutions of (2) and (4), for the same energy E , by P_1 and P_2 , the energies of the s -levels are given by the energies E for which

$$\left(\frac{P_1'}{P_1} \right)_{R_0} = \left(\frac{P_2'}{P_2} \right)_{R_0}.$$

In this way we have calculated the energies of the $1s$ and $2s$ levels, which are given in Table I:—

TABLE I.

	1s.	2	2p.
Potential hole of Fig. 6	- 1.87 eV.	- 0.54 eV.	- 0.61 eV.
Potential hole $-\epsilon^2/K_0r$	- 2.49 eV.	- 0.62 eV.	

For comparison we give also the energies for the first two levels, $n = 1$ and $n = 2$, in the coulomb potential hole $-\epsilon^2/K_0r$. In solving the wave equation for the p -states, $l = 1$, for $r \leq R_0$, it is more convenient to write

$$\psi = R(r)S_l(\theta, \phi),$$

where
$$\frac{d^2R}{dr^2} + \frac{2}{r} \cdot \frac{dR}{dr} + \left[\omega^2 - \frac{2}{r^2} \right] R = 0, \quad (5)$$

and the solution is

$$R = \frac{C}{\sqrt{\omega r}} J_{\frac{3}{2}}(\omega r).$$

The equation (1), with $l = 1$, is again solved numerically from $r = \infty$ up to $r = R_0$, and denoting these solutions by P_3 the energies of the p -states are then determined by the condition

$$\left(\frac{P_3'}{P_3} \right)_{R_0} - \frac{1}{R_0} = \left(\frac{R'}{R} \right)_{R_0}.$$

We have only determined the energy of the $2p$ level and its value is given in Table I. The wave functions for the $1s$, $2s$ and $2p$ levels are

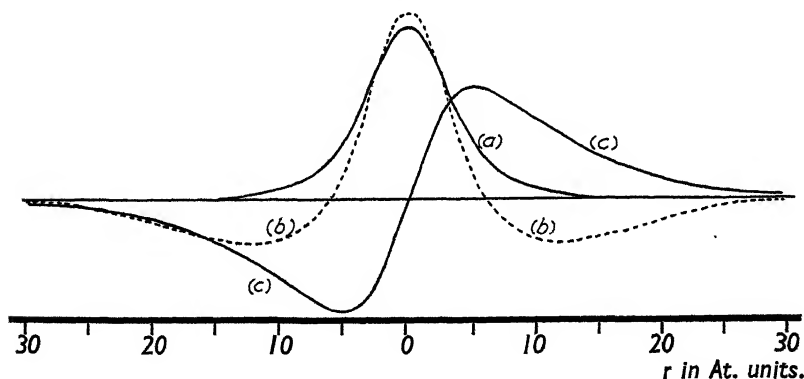


FIG. 7.—Wave functions for the stationary states of an F-centre :
(a) 1s, (b) 2s and (c) 2p.

shown in Fig. 7. It will be seen that the wave function for the ground level extends over the six neighbouring sodium ions; the higher levels have much larger orbits.

The oscillator strength for the $1s$ - $2p$ transition is

$$f_{sp} = \frac{8\pi^2 m (E_{2p} - E_{1s})}{h^2} |x_{sp}|^2,$$

where

$$|x_{sp}|^2 = |\int \psi(1s|r)\psi(2p|r)zd\tau|^2.$$

This gives

$$f_{sp} = 0.614.$$

For the hydrogen atom the corresponding oscillator strength is 0.46. Assuming the optical oscillator strength of the main F-band to be unity, the number of F-centres in the crystal can be determined from the absorption coefficient and half-band width. The number of excess atoms as determined chemically is found to be 1.24 times that determined optically. We therefore deduce that the oscillator strength of

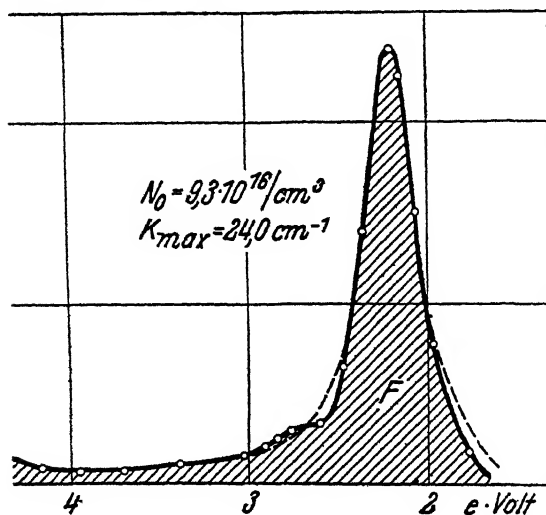


FIG. 8.

the main band is $1/1.24 = 0.81$. Also, the maximum of the F-band for NaCl corresponds to an energy of 2.72 eV., whereas with our simple model the energy of the $1s-2p$ transition is only ~ 1.26 eV.

It is seen, from Table I, that with our simple model the $2s$ and $2p$ levels have energies very near to that for the first excited level of the coulomb potential hole $-e^2/K_0 r$. In Fig. 8 we reproduce the F-band

for KCl as measured by Kleinschrod.²⁰ An attempt to analyse the band into its component lines shows that it is quite probable that the series limit of the line absorption lies about 0.8 eV. above the first peak.

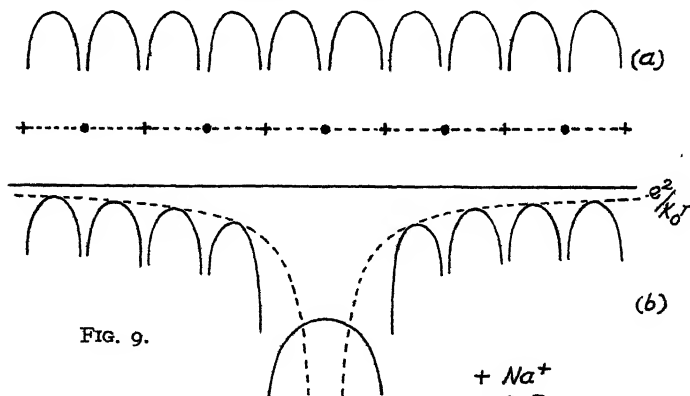


FIG. 9.

In the potential hole $-e^2/K_0 r$ with $K_0 = 2.17$, the value for KCl, the first excited level has an energy of -0.72 eV., which indicates that the excited levels of an F-centre are hydrogen-like, so that our results for the $2s$ and $2p$ levels are probably quite good. This means that, with the model we have chosen, the ground level has much too high an energy.

²⁰ F. G. Kleinschrod, *Ann. Physik*, 1936, 27, 97.

In order to obtain better agreement with experiment, in calculating the energy of the ground state it is necessary to take account of the ionic structure of the crystal.

In a perfect crystal the field is periodic with the period of the lattice, and along a line of alternate sodium and chlorine ions the potential energy of an electron will be as shown in Fig. 9a; when a negative ion is removed the potential energy of an electron will be somewhat as shown in Fig. 9b. The energy levels of the F-centre must approach a series limit, this limit being the energy of an electron which is just released from the potential hole and is free to move through the crystal, *i.e.* it is the energy χ ($= -0.5$ eV.) of the lowest conduction level of the crystal. Hence the effective depth of the potential hole, at the vacant lattice point, is

$$-\frac{\alpha e^2}{2a} + \frac{e^2}{R} \left(1 - \frac{1}{K_0}\right) - \chi.$$

At large distances, the potential energy of the electron will be

$$V = V_L - e^2/K_0 r,$$

where V_L is the potential energy of an electron in the perfect lattice. V_L is taken to be the spherically symmetrical function used in Part I in determining the wave function and energy of the lowest conduction level of the crystal. The wave equation to be satisfied by the wave function ψ of the electron is, for large distances from the vacant lattice point, using natural atomic units,

$$\nabla^2 \psi + 2 \left(E - V_L + \frac{1}{K_0 r} \right) \psi = 0. \quad (6)$$

We will denote the wave function of an electron in the lowest conduction level by ϕ_L , and its energy is taken to be zero since we are measuring the effective depth of the potential hole from the conduction level. Then ϕ_L satisfies the equation

$$\nabla^2 \phi_L - 2V_L \phi_L = 0.$$

Also, let $\psi = u_H$ be the solution, which tends to zero for large r , of

$$\nabla^2 \psi + 2 \left(E_H + \frac{1}{K_0 r} \right) \psi = 0.$$

Then the wave equation $\psi = \phi_L \cdot u_H$ satisfies the equation

$$\nabla^2 \psi + 2 \left(E_H - V_L + \frac{1}{K_0 r} \right) \psi = 2\phi_L \nabla_L \cdot \nabla u_H.$$

At large distances, ~ 20 At. units, $\nabla u_H \rightarrow 0$, and so $\psi = \phi_L \cdot u_H$ is a solution, of energy E_H , of equation (6). For small distances, $r \leq R_0$, the potential energy of the electron is taken to be constant and to have the value at the vacant lattice point, *viz.*, $-\frac{\alpha}{2a} + \frac{1}{R} \left(1 - \frac{1}{K_0}\right) - \chi$. At. units. Let $\psi = u_C$ be the solution, finite at the origin, of

$$\nabla^2 \psi + 2 \left[E_H + \frac{\alpha}{2a} - \frac{1}{R} \left(1 - \frac{1}{K_0}\right) + \chi \right] \psi = 0$$

for $r \leq R_0$. We assume that ϕ_L, u_H is a solution of (6) for all $r > R_0$, and hence the energy levels are determined by the boundary condition,

$$\left(\frac{u'_G}{u_G}\right)_{R_0} = \left(\frac{\phi'_L}{\phi_L} + \frac{u'_H}{u_H}\right)_{R_0}.$$

ϕ_L was taken to be the wave function obtained in Part I for an electron in the lowest conduction level, and the equations for u_H and u_G were solved as before. The theoretical inter-ionic distance used in calculating ϕ_L was $2a = 8.0$ At. units. Now the radii of the Cl^- and Na^+ ions in NaCl are ~ 1.81 Å and ~ 0.98 Å respectively. Since the hole in the lattice is due to the removal of a Cl^- ion we choose the value of R_0 to be $\sim \frac{1.81}{1.81 + 0.98} \times 8.0 = 5.0$ At. units. For this value of R_0 the energy of the ground state is -3.5 eV. (below the conduction level). For the energy of the $2p$ level, using only the functions u_G and u_H , as in the first model, we obtain the value -1.0 eV. This gives an energy of 2.5 eV. for the $1s-2p$ transition, which is in good agreement with the experimental value of 2.72 eV.

I wish to thank Prof. Mott, under whose direction this work has been carried out, for his invaluable advice and assistance.

Summary.

In Part 1 Slater's extension of the method of Wigner and Seitz is used to calculate the energy of the lowest conduction level in NaCl , and to determine the width of the first band of allowed conduction levels for the (100) direction. Part 2 describes attempts to ascribe to an electron at a vacant, negative-ion lattice point wave functions which give rise to energy levels which are in agreement with the experimental data on F-centres.

*H. H. Wills Physics Laboratory,
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THE QUATERNARY SYSTEM $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$ AT 25°C .

BY F. E. JONES.

Received 30th August, 1939.

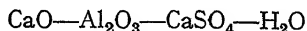
In the chemistry of Portland and aluminous cements the conditions of formation and properties of calcium sulphoaluminates are of particular interest. Such compounds may arise during the setting of Portland cement and by the action of sulphate waters on concrete. The disintegrating effect of such waters on Portland cement concrete is generally considered to be mainly due to the formation of a sulphoaluminate crystallising in long needles, and having the composition



This compound, the composition of which was first established by

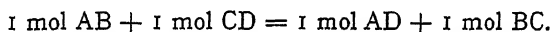
Michaelis¹ has been described subsequently by a number of workers. Another calcium sulphoaluminate has been described by Lerch, Ashton and Bogue² as crystallising in hexagonal plates, and corresponding to the formula $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12 \text{H}_2\text{O}$. Subsequently Forsén³ and Mylius⁴ also obtained this compound. Foret⁵ concludes that no low sulphate form exists. The present writer⁶ has, however, obtained well-defined crystals of refractive indices identical with those found by Lerch, Ashton and Bogue, by the conversion of the high sulphate form in aqueous solution at 100° C.

In order to determine the precise conditions of formation of the calcium sulphoaluminates, a study of the quaternary system

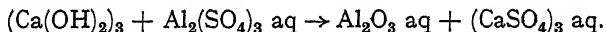


has been undertaken at the Building Research Station. Hitherto, only a limited amount of work has been carried out by a few authors, including the present writer, involving the determination of the concentrations of solutions obtained in mixes of the high sulphate form of calcium sulphoaluminate and lime and calcium sulphate solutions of various concentrations, and the meaning of the results obtained has remained obscure.

The method adopted in this investigation has been to consider the system as being formed by reciprocal salt pairs.⁷ It is essential in this method of representation that the compositions of mixtures be expressed in molecular percentages, and also that the four salts shall be related by the equation:—



The salt pairs involved are $\text{Ca}(\text{OH})_2$ and $\text{Al}_2(\text{SO}_4)_3$ aq, and Al_2O_3 aq and CaSO_4 aq. The following reaction occurs:—



The plane Jänecke projection of the space figure by lines radiating from the water point will be contained within the square shown in Fig. 11a. Results of the present work are shown projected thus in Figs. 11a and 11b.

The equilibria data obtained naturally depend upon the nature of the solid phases considered. Thus, crystalline calcium hydroxide obtained by recrystallisation from a lime solution has an appreciably lower solubility than the calcium hydroxide got from the slaking of lime obtained by heating calcium compounds such as the carbonate or oxalate. In all equilibria involving the hydroxide it is therefore necessary to define the form of lime used as strictly as possible. Crystalline $\text{Ca}(\text{OH})_2$ as obtained from solution is to be regarded as the fundamental stable form, which is quite definite and reproducible and the

¹ W. Michaelis, *Tonind. Ztg.*, 1892, 105.

² W. Lerch, F. W. Ashton and R. H. Bogue, *U.S.B. Stand. J. Research*, 1929, 2, 715.

³ L. Forsén, *Zement*, 1933, 22, 73, 87, 100.

⁴ C. Mylius, *The calcium aluminate hydrates and their double salts* (*Act. Acad. Aboensis*, 1933, vii, 3).

⁵ J. Foret, *Compounds of calcium salts and calcium aluminates*, Paris, 1935, Hermann et Cie, pp. 68.

⁶ F. E. Jones, *Symp. Chem. Cements*, Stockholm, 1938, 231.

⁷ See, for example, *The Principles of the Phase Theory*, D. A. Clibbens. MacMillan & Co., 1920.

other more soluble forms as metastable with respect to it and showing a greater or less tendency to change to the stable form. Similar considerations apply to hydrated alumina, according as we consider the crystalline or gel form. While in pure water the solubilities of both forms are very small, the solubility of the crystalline alumina must be even smaller than that of the gel. In solutions containing lime, appreciable concentrations of alumina are obtained with gel as solid phase, while the writer has found that with crystalline alumina $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ much less is taken into solution.

With respect to the quaternary system, what may be regarded as the fundamental system is that which includes crystalline $\text{Ca}(\text{OH})_2$ and crystalline $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ as the solid phases. In cement chemistry it is, however, necessary to consider equilibria involving higher lime concentrations than can be attained by crystalline $\text{Ca}(\text{OH})_2$, and also equilibria involving alumina gel, metastable with respect to the crystalline forms of lime and alumina. The present paper represents a compromise. Equilibria involving lime as solid phase are here restricted to crystalline $\text{Ca}(\text{OH})_2$, while the gel form of alumina only is considered. These were selected because of the instability of supersaturated lime solutions and the relative stability of the metastable gel form of alumina. Further work is in progress to supplement these data by using a more soluble form of lime and crystalline alumina respectively.

The following shorthand notation has been used in writing certain formulæ: $\text{CaO} = \text{C}$, $\text{Al}_2\text{O}_3 = \text{A}$.

Experimental.

The method of investigation adopted in the present work was as follows. Trial mixtures of solutions of calcium sulphate, calcium hydroxide, and aluminium sulphate, with alumina gel, solid $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, crystalline $\text{Ca}(\text{OH})_2$, $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ or $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ were made up in appropriate combinations corresponding to the various boundary curves and invariant points examined. The volume of the solution phase was 125 ml. The mixes were contained in large Pyrex glass test-tubes, 32 mm. by 200 mm., with rim, closed with a rubber stopper. These were placed horizontally on a rocking shaker immersed in a water thermostat at 25°C . The shaker oscillated through an angle of about 45° once every second. Shaking was continued for periods of 7 and 28 days before filtration. It may be stated that in general the 7 and 28 day data on identical mixes show only small differences, and fall on the same curves. It seems, therefore, probable that any departure of the data from true equilibrium values is slight. In order to avoid contamination by carbon-dioxide as much as possible, filtration was in most cases made by means of the arrangement shown in Fig. 1a, so that there was protection against the carbon dioxide of the room during the short period of filtration. In the case of mixes containing alumina gel, filtration in this way was tedious, and there was risk of disturbance of the equilibrium set up at 25°C . by prolonged filtration at the lower temperature of the room. It was found best to allow such mixes to stand in the bath overnight before filtration, so that the solid residue including alumina gel settled to the bottom. Except in the case of mixes involving $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ a clear supernatant solution was formed which was filtered into a pipette while standing in the bath, using the arrangement shown in Fig. 1b. The small amount of solid and solution remaining was then filtered as described above through either a small Hirsch or Büchner type funnel. In the case of $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ mixes the supernatant liquid usually still contained suspended solid, and it was found best to remove this liquid by a pipette and to filter separately from the residual solid

through a small Büchner funnel. After filtration, the solutions were transferred to weighed Pyrex glass flasks, weighed, and made slightly acid to methyl red with HCl. The solid residues were dried *in vacuo* in a small desiccator containing a saturated solution of ammonium sulphate (V.P. approximately 14 mm. at room temperature). They were then examined with the petrographic microscope by the immersion method in order to determine the solid phases. When this examination showed the presence of the solid phases corresponding to the boundary curve or invariant point sought, the solution was analysed for Al_2O_3 , CaO, and SO_3 . When a second or third solid phase was absent, the mix was modified until the desired solid phases were obtained.

Analyses were made gravimetrically. Owing to the difficulty of obtaining accurate and reproducible results in these analyses, as evidenced in the literature, it is desirable to describe briefly the conditions of the determinations. For alumina, the solutions were concentrated to about 50 ml. except where high concentrations of calcium sulphate precluded this. Ammonium chloride was added to give an approximately 2.5 per cent. solution, and the boiling solution made slightly alkaline to methyl

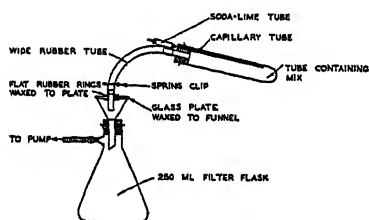


FIG. 1a.—Showing arrangement for filtration with protection against carbon dioxide.

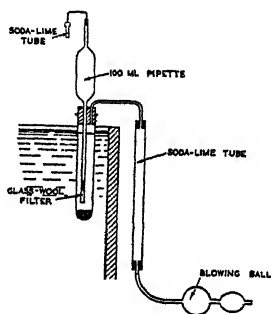


FIG. 1b.—Showing arrangement for filtration in thermostat.

red with 5N. ammonium hydroxide. Appreciable amounts of alumina were separately re-dissolved and again precipitated. The precipitated gel was ignited in gold-palladium alloy crucibles at 1000°C . in an electric furnace for two periods of about one hour each. For this and the other ignited precipitates, cooling was effected for half-an-hour in a small desiccator, the bottom half of which contained a small amount of soda-lime to take up any carbon-dioxide while the top half in which the crucibles were placed contained phosphorus pentoxide. Lime was determined in the filtrate after precipitating alumina. The solution was ordinarily concentrated to about 50 ml., and a slight excess of solid powdered ammonium oxalate added to the hot solution. The solution was kept hot for about half-an-hour, allowed to cool, and filtered after not less than two hours. The precipitate was washed with about 25 ml. of a cold 0.1 % solution of ammonium oxalate (made slightly alkaline with ammonia) and ignited at 1000°C . as for the alumina. Sulphate was determined in the filtrate after precipitating lime. The solution was either concentrated or diluted as necessary to give a volume of about 25 ml. or a concentration corresponding to not more than 0.15 g. BaSO_4 to 100 ml. of solution. Concentrated hydrochloric acid was added in the proportion of 1 ml. acid to 100 ml. solution. After heating to boiling, hot 0.1 N. barium chloride solution was added slowly in the proportion of 15 ml. to every 0.1 g. BaSO_4 . The solution was kept hot for not less than half-an-hour, and filtered after standing overnight. Any appreciable amount

of precipitate was first washed a few times by decantation with hot water. The precipitate and filter paper were then washed with hot water until the filtrate was substantially free from opalescence when tested with silver nitrate solution. Ignition was made at 900°C . the temperature being raised fairly gradually to this value.

The procedures described are convenient and lead to concordant results, but there are slight divergences from the true values, for which it is necessary to apply corrections. Owing to retention of water by the alumina precipitate even at 1000°C . the results are slightly too high, and a correction of 1 per cent. of the weighed amount of alumina has been made to allow for this. The weighing of lime as oxide also leads to slightly high results, owing to the ease with which traces of moisture are absorbed, whilst the procedure adopted for the sulphate precipitation tends to give low results.

In order to determine what corrections it would be necessary to apply in the last two cases, analyses were made by the procedures indicated on re-crystallised calcium sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as standard. The results obtained are given in Table I.

TABLE I.

Weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. (g.)	Weight of CaO (theory). (g.)	Weight of CaO found. (g.)		Weight of SO_3 (theory). (g.)	Weight of SO_3 found as BaSO_4 . (g.)
		As CaCO_3 .	As CaO .		
0.0785	0.0255	0.0256	0.0258	0.0365	0.0365
0.0747	0.0243	0.0246	0.0245	0.0348	0.0348
0.3107	0.1010	0.1010	0.1020	—	—
0.3158	0.1026	0.1031	0.1040	—	—
0.3096	0.1005	0.1009	0.1018	0.1441	0.1430
0.3096	0.1005	0.1011	0.1019	0.1441	0.1430

Weighings of CaO as CaCO_3 were made after careful ignition of the calcium oxalate precipitate at $550-570^\circ$. Even in this case the values obtained are slightly too high. Since the determination as CaO made for quicker working owing to the absence of need for a carefully controlled temperature, this procedure was adopted. The table shows that the resultant values are too high by 1 per cent. of the weight of CaO found, and accordingly this correction has been applied to the values obtained during the course of the work.

In the case of sulphate, the data indicate that for small amounts of sulphate there is good agreement between theoretical and found values. For larger amounts of sulphate, the values found are low. A correction of 1 per cent. of the weight of sulphate found has been applied to all weights of barium sulphate amounting to more than the equivalent of 0.1 g. of SO_3 .

Materials.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.—"Pure precipitated" calcium sulphate was re-crystallised. Analysis gave $\text{K}_2\text{O} = \text{nil}$, $\text{Na}_2\text{O} = 0.02$ per cent.

$\text{Ca}(\text{OH})_2$.—Crystalline $\text{Ca}(\text{OH})_2$ was prepared by boiling, with protection from CO_2 , a saturated solution made with CaO obtained by the ignition of "Analar" CaCO_3 at 1000°C . Well-defined prisms and thick hexagonal plates of $\text{Ca}(\text{OH})_2$ of a size suitable for microscopic examination were obtained. The prisms varied from about 45 to 65μ in length by about 30μ in breadth. The plates varied from about 40 to 60μ in diameter.

$\text{Al}_2(\text{SO}_4)_3$ aq.—The aluminium sulphate ordinarily used for the preparation of solutions for mixes was an "Analar" brand. This gave a clear solution in water, but analysis showed a $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio rather less than 3. $\text{Al}_2\text{O}_3 = 17.1$ per cent., $\text{SO}_3 = 37.25$ per cent., $\text{SO}_3/\text{Al}_2\text{O}_3 = 2.78$. No iron was detected, and alkalis amounted to 0.12 per cent. NaKO. Within the quaternary system the departure from the 3:1 ratio is of little importance. For work on the ternary system



the product was re-crystallised and dried *in vacuo* over saturated ammonium sulphate solution to constant weight. Analysis $\text{Al}_2\text{O}_3 = 16.3$ per cent., $\text{SO}_3 = 37.3$ per cent., $\text{SO}_3/\text{Al}_2\text{O}_3 = 2.91$.

$3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ H}_2\text{O}$.—The preparation of $\text{C}_3\text{A} \cdot 6 \text{ H}_2\text{O}$ which shall be both pure and of good crystal form so as to facilitate microscopic examination is a matter of considerable difficulty. The conditions leading to a satisfactory product from both these points of view are not properly understood. The $\text{C}_3\text{A} \cdot 6 \text{ H}_2\text{O}$ ordinarily used was prepared as described by Thorvaldson and Grace,⁸ by autoclaving in steam for periods up to 7 days, 1 to 2 g. lots of C_3A in a small autoclave of 100 ml. capacity at a gauge pressure which was varied in different preparations from 60 to 150 lb. per sq. in. The C_3A was prepared by heating at 1400–1450° C. with intermediate recrushing a mixture of CaCO_3 and Al_2O_3 , and gave on analysis $\text{CaO} = 61.3$ per cent., $\text{Al}_2\text{O}_3 = 38.7$ per cent.; insoluble in dilute $\text{HCl} = 1.0$ per cent., $\text{CaO}/\text{Al}_2\text{O}_3 = 2.9/1$. Microscopic examination showed the insoluble material to be mainly quartz apparently introduced during crushing in an agate mortar. The $\text{C}_3\text{A} \cdot 6 \text{ H}_2\text{O}$ on microscopic examination showed irregular grains of varying size, often in clusters, isotropic, refractive index $1.605 \pm .003$. There was a small amount of impurity consisting of quartz and traces of CaCO_3 . Few or no well-developed crystal forms were obtained, but the product was satisfactory from the point of view of microscopic examination in that it contained no hexagonal plate forms. In certain mixes, $\text{C}_3\text{A} \cdot 6 \text{ H}_2\text{O}$ prepared by the method of Travers and Zahabi⁹ was used. The product so obtained was very fine-grained and contained a small amount of birefringent material. Analysis of one preparation gave $\text{CaO} = 43.8$ per cent., $\text{Al}_2\text{O}_3 = 26.65$ per cent., insoluble in $\text{HCl} = 0.2$ per cent., $\text{CaO}/\text{Al}_2\text{O}_3 = 3.00$.

$2 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8 \text{ H}_2\text{O}$ was prepared by the method of Koyanagi.¹⁰ Elutriated aluminous cement was shaken with water, and the product washed with alcohol on a sieve. The small balls of $\text{C}_2\text{A} \cdot 8 \text{ H}_2\text{O}$ retained on the sieve were combined from several preparations and analysed. Found $\text{CaO} = 31.15$ per cent., $\text{Al}_2\text{O}_3 = 27.0$ per cent. (theory $\text{CaO} = 31.3$ per cent., $\text{Al}_2\text{O}_3 = 28.5$ per cent.). Loss on ignition = 40.9 per cent., insoluble in dilute $\text{HCl} = 0.65$ per cent., $\text{CO}_2 = 0.6$ per cent. Microscopic examination of the crushed balls showed broken spherulitic clusters of plates on edge, with indices $w = 1.523 \pm .003$, $\epsilon = 1.510$. Various authors give the values $w = 1.520 \pm .002$, $\epsilon = 1.505 \pm .003$.

$3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ CaSO}_4 \cdot 32 \text{ H}_2\text{O}$.—The material used in this work was prepared at room temperature by the addition of limewater to aluminium sulphate solution containing excess calcium sulphate to stabilise the $\text{C}_3\text{A} \cdot 3 \text{ CaSO}_4 \cdot 32 \text{ H}_2\text{O}$. Precautions were taken to avoid contamination by carbon dioxide. The product was free from carbonate and gave on analysis $\text{CaO} = 26.65$ per cent., $\text{Al}_2\text{O}_3 = 8.2$ per cent., $\text{SO}_3 = 19.2$ per cent. (theory $\text{CaO} = 26.8$ per cent., $\text{Al}_2\text{O}_3 = 8.15$ per cent., $\text{SO}_3 = 19.15$ per cent.). The refractive indices were $w = 1.465 \pm .003$, $\epsilon = 1.460 \pm .003$.

⁸ T. Thorvaldson and N. S. Grace, *Can. J. Res.*, 1929, 1, 36–47.

⁹ A. Travers and H. Zahabi, *Comptes Rendus*, 1937, 205, 1407.

¹⁰ K. Koyanagi, *Concrete*, 1932, 40 (8), 40–46.

Results.

I. The Ternary Systems.

The four ternary systems involved are :—

- (i) $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}$.
- (ii) $\text{H}_2\text{O}-\text{CaO}-\text{CaSO}_4$.
- (iii) $\text{H}_2\text{O}-\text{CaSO}_4-\text{Al}_2(\text{SO}_4)_3$.
- (iv) $\text{H}_2\text{O}-\text{Al}_2(\text{SO}_4)_3-\text{Al}_2\text{O}_3$.

(i) **The Ternary System $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}$.**—A very considerable amount of work has been carried out by many authors in connection with this system, though without reaching any definite conclusion. A discussion of previous work in this field is given by Bessey.¹¹ A full investigation of the system at 25°C . has been made by Lea and Bessey¹² over a period of several years, and their results are given in Fig. 2, which is the simple ternary representation of the system within an equilateral triangle. Stable equilibria are represented by curves (a) and (b) for Al_2O_3 aq.* and $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ respectively. The point D is the invariant point

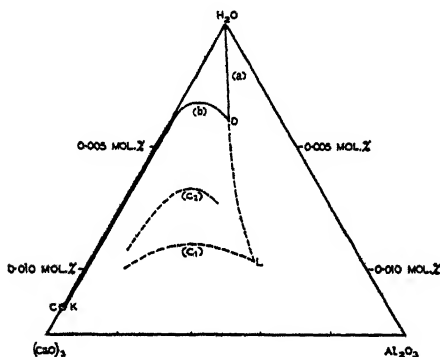


FIG. 2.—Ternary system.
 $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}$
(Lea and Bessey).

Al_2O_3 aq— $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$. It is not clear whether point K is an invariant point for $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}-\text{C}_4\text{A} \cdot 13\text{H}_2\text{O}$ or $\text{C}_3\text{A} \cdot 12\text{H}_2\text{O}-\text{C}_4\text{A} \cdot 13\text{H}_2\text{O}$. This point K is practically identical with the solubility of crystalline $\text{Ca}(\text{OH})_2$ as determined in this work (point C). It thus appears doubtful whether up to the maximum concentration possible with crystalline $\text{Ca}(\text{OH})_2$, C_4A aq has a stable existence. As regards metastable equilibria, the metastable $\text{C}_2\text{A} \cdot 8\text{H}_2\text{O}$ curve falls within the limits (C_1) and (C_2) . Point L appears to be the metastable invariant point Al_2O_3 aq— $\text{C}_2\text{A} \cdot 8\text{H}_2\text{O}$. In both cases, $\text{C}_2\text{A} \cdot 8\text{H}_2\text{O}$ ceases to exist in the ternary system in solutions of high lime concentration, and curves (C_1) and (C_2) disappear.

(ii) **The Ternary System $\text{H}_2\text{O}-\text{CaO}-\text{CaSO}_4$.**—The ternary system $\text{H}_2\text{O}-\text{CaO}-\text{CaSO}_4$ has been investigated by Cameron and Bell¹³ at 25°C . Their data, recalculated for the purposes of the present method of representation are plotted in Fig. 3. The data were obtained after shaking the solutions for two weeks in a thermostat. Data obtained during the present investigation for the solubility of recrystallised $\text{Ca}(\text{OH})_2$ in water and in calcium sulphate solutions, the invariant point $\text{Ca}(\text{OH})_2-\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and for the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water are given in Table II. In order to save space, in this and subsequent tables, only selected data sufficient to define the positions of the boundary curves

¹¹ G. E. Bessey, *Symp. Chem. Cements*, Stockholm, 1938, 178.

¹² F. M. Lea and G. E. Bessey, *Private communication*.

* Gel form. The solubility curve with respect to crystalline $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ must fall below this.

¹³ F. K. Cameron and J. M. Bell, *J. Am. Chem. Soc.*, 1906, 28, 1220.

are given. All the available data, however, are plotted in the figures. The invariant point composition in grams per 1000 g. solution was found to be $\text{CaO} = 1.745$, $\text{SO}_3 = 0.998$. The data obtained are plotted in Fig. 3. As compared with Cameron and Bell's results, there is a pronounced shift in the position of the $\text{Ca}(\text{OH})_2$ boundary curve, and the $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2\text{—CaSO}_4 \cdot 2\text{H}_2\text{O}$ invariant points. The mean of 9 determinations of the solubility of recrystallised $\text{Ca}(\text{OH})_2$ with shaking periods varying from 1 to 28 days was 0.0116 mol. per cent. $(\text{CaO})_s$, or 1.08 g. CaO per 1000 g. solution. The deviation from the mean value is in 6 cases not more than 0.0001 mol. per cent., and the value given appears to be substantially correct. The value obtained is appreciably lower than any which have been found in the literature. Thus Bassett¹⁴ for crystalline $\text{Ca}(\text{OH})_2$ obtained by heating limewater reports a solu-

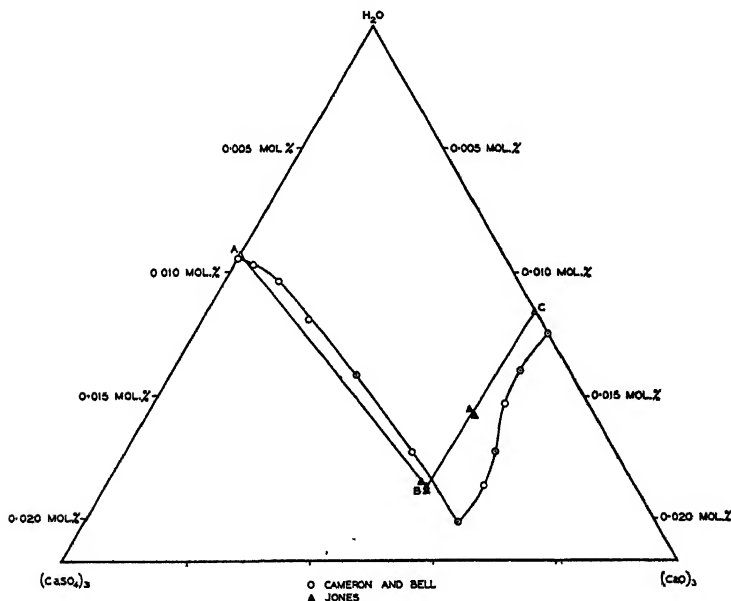


FIG. 3.—Ternary system. $\text{H}_2\text{O—CaO—CaSO}_4$.

bility of 1.13 g. CaO per 1000 g. solution, whilst Johnstone and Grove¹⁵ for coarsely crystalline $\text{Ca}(\text{OH})_2$ got 1.11 g. CaO per 1000 g. solution.

(iii) **The Ternary System $\text{H}_2\text{O—CaSO}_4\text{—Al}_2(\text{SO}_4)_3$.**—No data appear to be available on the system $\text{H}_2\text{O—CaSO}_4\text{—Al}_2(\text{SO}_4)_3$. Accordingly, two determinations of the solubility of calcium sulphate in dilute solutions of aluminium sulphate have been made, sufficient to establish the portion of this system required for the present investigation. The data are given in Table III. The aluminium sulphate used contained Al_2O_3 in excess of the ratio $\text{SO}_3/\text{Al}_2\text{O}_3 = 3$. Actual ratio $\text{SO}_3/\text{Al}_2\text{O}_3 = 2.91$. There is on this account a slight deviation from the $\text{H}_2\text{O—}(\text{CaSO}_4)_s\text{—Al}_2(\text{SO}_4)_s$ plane.

(iv) **The Ternary System $\text{H}_2\text{O—Al}_2(\text{SO}_4)_3\text{—Al}_2\text{O}_3$** has been investigated by Kremann and Hüttinger.¹⁶ It is involved in a part of the quaternary system which is not of direct interest in cement chemistry, and has therefore not been considered in the present investigations.

¹⁴ H. Bassett, *J. Chem. Soc.*, 1934, 1270.

¹⁵ J. Johnstone and C. Grove, *J. Am. Chem. Soc.*, 1931, 53, 3976.

¹⁶ Kremann and Hüttinger, *Jahrb. K. K. Geologischen, Reichsanstalt*, 1908, 58, 637.

TABLE II.—THE TERNARY SYSTEM $\text{H}_2\text{O}-\text{CaO}-\text{CaSO}_4$.

No.	Time Shaken (Days).	Composition of Initial Mix.	Solid Phases.	G. mols. $\times 10^4$ per 1000 g. Solution.		Total g. mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(\text{CaSO}_4)_s$.	Mol. % $(\text{CaO})_s$.	Mol. % Total Salts in Solution
				$(\text{CaSO}_4)_s$.	$(\text{CaO})_s$.				
N ₃	7	125 ml. water, 0.500 g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	51.2	—	51.2	100	0	0.00923
N ₄	28	As N ₃	"	51.1	—	51.1	100	0	0.00921
FI ₄	7	125 ml. water, 0.331 g. $\text{Ca}(\text{OH})_2$ (0.250 g. CaO), 0.316 g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (0.250 g. CaSO_4)	(i) $\text{Ca}(\text{OH})_2$ (ii) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	41.5	62.6	104.1	39.9	60.1	0.01875
FI _{4a}	28	As FI ₄	"	41.5	63.1	104.6	39.7	60.3	0.01885
AI to A ₄	7 and 28	125 ml. CaO soln. (1.065 g./l.), 0.100 g. $\text{Ca}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	—	64.3	64.3	0	100	0.0116
A ₅ to A ₉	1, 7, 28	125 ml. water, 0.280 g. $\text{Ca}(\text{OH})_2$.							

TABLE III.—THE TERNARY SYSTEM $\text{H}_2\text{O}-\text{CaSO}_4-\text{Al}_2(\text{SO}_4)_3$.
SOLUBILITY CURVE AI: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

No.	Time Shaken (Days).	Preparation of Initial Mix.	Solid Phases.	g.-mol. $\times 10^4$ per 1000 g. Solution.			Total g.-mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(\text{CaSO}_4)_s$.	Mol. % Al_2O_3 .	Mol. % $\text{Al}_2(\text{SO}_4)_3$.	Mol. % Total Salts in Solution.
				$(\text{CaSO}_4)_s$.	Al_2O_3 .	$\text{Al}_2(\text{SO}_4)_3$.					
F ₃₁	28	125 ml. water, 0.379 g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.343 g. $\text{Al}_2(\text{SO}_4)_3$ aq.*	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	47.0	1.5	42.6	91.1	51.6	1.65	46.75	0.01641
F ₃₂	28	125 ml. water, 0.379 g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.098 g. $\text{Al}_2(\text{SO}_4)_3$ aq.	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	49.8	.9	11.7	62.4	79.8	1.45	18.8	0.01125

* 16.3 % Al_2O_3 , 37.3 % SO_3 .

II. The Quaternary System.

In working out the quaternary system, it has been considered in relation to the stable and metastable equilibria of the ternary system $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}$ as determined by Lea and Bessey. It has already been indicated that the only stable ternary compound in this system is $\text{C}_2\text{A} \cdot 6\text{H}_2\text{O}$, except for $\text{C}_4\text{A} \cdot 13\text{H}_2\text{O}$ which may have a stable existence in solutions of very high lime concentration. The formation of the stable $\text{C}_2\text{A} \cdot 6\text{H}_2\text{O}$ by crystallisation from solution in the ternary system has proved to be a matter of considerable difficulty, and in determining the corresponding boundary curve in the quaternary system, the method adopted has been to add prepared $\text{C}_2\text{A} \cdot 6\text{H}_2\text{O}$ to the mix and to involve it in a reaction designed to give partial conversion to a second solid phase. As regards metastable equilibria attention has been confined to equilibria with $\text{C}_2\text{A} \cdot 8\text{H}_2\text{O}$, and a similar method of approach has been used. The

only quaternary compound found has been the high sulphate form of calcium sulphoaluminate $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$.

The following boundary curves and invariant points have been determined:—

(a) *Boundary Curves.*

- (1) $CaSO_4 \cdot 2 H_2O - Al_2O_3$ aq. (JE).*
- (2) Al_2O_3 aq— $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (EH).
- (3) $CaSO_4 \cdot 2 H_2O - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (EF).
- (4) $Ca(OH)_2 - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (FG).
- (5) $C_3A \cdot 6 H_2O - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (GH).
- (6) $C_3A \cdot 6 H_2O - Al_2O_3$ aq. (HD).
- (7) $C_3A \cdot 8 H_2O - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (MN).
- (8) $C_3A \cdot 8 H_2O - Al_2O_3$ aq. (NL).

(b) *Invariant Points.*

- (1) $CaSO_4 \cdot 2 H_2O - Al_2O_3$ aq— $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (E).
- (2) $CaSO_4 \cdot 2 H_2O - Ca(OH)_2 - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (F).
- (3) $Ca(OH)_2 - C_3A \cdot 6 H_2O - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (G).
- (4) $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O - C_3A \cdot 6 H_2O - Al_2O_3$ aq. (H).
- (5) $Ca(OH)_2 - C_3A \cdot 8 H_2O - C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. (M).
- (6) $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O - C_3A \cdot 8 H_2O - Al_2O_3$ aq. (N).

TABLE IV.—BOUNDARY CURVE JE : $CaSO_4 \cdot 2 H_2O - Al_2O_3$ aq.

No.	Time Shaken (Days).	Preparation of Initial Mix.	Solid Phases.	g. mol. $\times 10^4$ per 1000 g. Soln.			Total g. mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(CaSO_4)_s$.	Mol. % $(CaO)_s$.	Mol. % Al_2O_3 .	Mol. % Total Salts in Solution.
				$(CaSO_4)_s$.	$(CaO)_s$.	Al_2O_3 .					
F11	7	51.5 ml. water, 0.379 g. $CaSO_4 \cdot 2 H_2O$, 50 ml. $Al_2(SO_4)_3$ soln. containing 0.0725 g. Al_2O_3 , 0.1525 g. SO_3 . Shaken 1 day. 23.5 ml. CaO soln. (0.025 g. CaO) added.	(i) $CaSO_4 \cdot 2 H_2O$ (ii) Al_2O_3 aq.*	43.6	2.25	40.8	86.65	50.3	2.6	47.2	0.01563
F29	28	101.5 ml. $CaSO_4$ soln. (0.209 g. $CaSO_4$), 0.115 g. $CaSO_4 \cdot 2 H_2O$, 0.416 g. $Al_2(SO_4)_3$ aq.† Shaken 3 days. 23.5 ml. CaO soln. (0.025 g. CaO) added.	As above	44.3	4.1	38.9	87.3	50.8	4.7	44.6	0.01575
F10	7	As F11, but 76.5 ml. water, 25 ml. $Al_2(SO_4)_3$ soln.	As above	48.9	0.35	11.7	60.95	80.3	0.55	19.2	0.01100
F23	28	As F29; but 0.213 g. $Al_2(SO_4)_3$ aq. Shaken 1 day.	As above	49.5	0.85	10.7	61.05	81.1	1.4	17.5	0.01102

* Initial refractive index < 1.47 rose on ageing to 1.48–1.49.

† 17.1 % Al_2O_3 , 37.25 % SO_3 .

With regard to the above it is to be noted that in the boundary curves 7 and 8 and invariant points 5 and 6, metastable $C_3A \cdot 8 H_2O$ is substituted for the stable $C_3A \cdot 6 H_2O$ of the boundary curves 5 and 6 and invariant points 3 and 4. For curves 6 and 8 no data have been obtained on the

* The lettering refers to the appropriate curves in the Figs. or Plate 1.

actual curves, but these are short and sufficiently defined by the invariant points.

The Boundary Curve $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ aq. (JE.)—The relevant data, including the preparation of the initial mix, the solid phases, and the concentrations of solutions are given in Table IV. The alumina gel, present as second solid phase with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, dried out after filtration to a horny mass with conchoidal fracture. The index rose gradually on ageing from an initial value of less than 1.47 to a final value of 1.48–1.49.

TABLES V–X.

No.	Time Shaken (Days).	G. mol. $\times 10^4$ per 1000 g. Solution.			Total g. mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(\text{CaSO}_4)_s$	Mol. % $(\text{CaO})_s$	Mol. % Al_2O_3	Mol. % Total Salts in Solution.
		$(\text{CaSO}_4)_s$	$(\text{CaO})_s$	Al_2O_3					

Table 5.—Invariant point E :

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ aq.— $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (Mixes H20, H28.)

Boundary Curve EH :

Al_2O_3 aq.— $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (Other mixes.)

H20	7	51.3	0.25	0.7	52.25	98.2	0.5	1.35	0.00942
H28									
(repeat H20)	28	53.8	0.65	0.5	54.95	98.0	1.2	0.9	0.00990
H18	7	51.3	0.65	1.65	53.6	95.7	1.2	3.1	0.00983
H15	7	40.1	0.7	0.85	41.65	96.3	1.7	2.05	0.00750
H29	28	14.9	1.2	1.35	17.45	85.4	6.9	7.7	0.00315
H31									
(repeat H24 *)	28	5.3	3.35	2.45	11.1	47.8	30.2	22.1	0.00200
H27	7	1.9	5.4	3.5	10.8	17.6	50.0	32.4	0.00195
H33									
(repeat H27)	28	3.1	4.3	2.65	10.05	30.8	42.8	26.4	0.00181
H67									
(repeat H66)	28	1.7	5.95	3.05	10.7	15.9	55.6	28.5	0.00193
H38	7	0.3	12.05	7.85	20.2	1.5	59.7	38.9	0.00364

* This, and other points, for which data are not given, are shown in Figs. 11a and 11b.

Table 6.—Boundary Curve EF :

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (Mixes F8, F19, F9, F6, F25, F1.)

Invariant Point F :

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (Mixes F18, F26).

Boundary Curve FG :

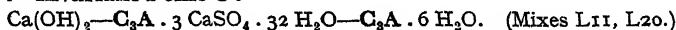
$\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (Mixes F12, F22, F13, F15, F27, G6).

F19									
(repeat F8)	28	50.1	2.1	0.3	52.5	95.5	4.0	0.6	0.00947
F25	28	46.1	20.9	0.15	67.15	68.7	31.1	0.2	0.01211
F1	7	42.7	46.6	0.3	89.6	47.6	52.0	0.35	0.01615
F18	7	40.8	64.0	0.6	105.4	38.7	60.7	0.6	0.01900
F26									
(repeat F18)	28	41.3	64.2	0.6	106.1	38.9	60.5	0.6	0.01913
F22	28	23.3	62.9	0.5	86.7	26.9	72.6	0.55	0.01562
F13	7	11.3	64.2	0.15	75.65	15.0	84.9	0.2	0.01364
F27									
(repeat F15)	28	2.6	61.3	0.15	64.05	4.1	95.7	0.25	0.01155
G6	7	0.5	59.9	0.15	60.55	0.8	99.0	0.25	0.01092

TABLES V-X.—Continued.

No.	Time Shaken (Days).	G. mol. $\times 10^4$ per 1000 g. Solution.			Total g. mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(\text{CaSO}_4)_s$.	Mol. % $(\text{CaO})_s$.	Mol. % Al_2O_3 .	Mol. % Total Salts in Solution.
		$(\text{CaSO}_4)_s$.	$(\text{CaO})_s$.	Al_2O_3 .					

Table 7.—Invariant Point G:



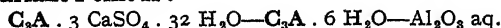
Boundary Curve GH:



L11	7	0.75	64.1	—	64.85	1.15	98.9	—	0.01170
L20									
(repeat L11)	28	0.45	62.4	0.15	63.0	0.7	99.1	0.25	0.01136
L8									
(repeat L4)	28	0.6	41.7	—	42.3	1.4	98.6	—	0.00764
L7									
(repeat L3)	28	0.8	27.3	—	28.1	2.85	97.1	—	0.00507
L6									
(repeat L2)	28	1.0	13.05	0.4	14.45	6.9	90.3	2.75	0.00261
L12	7	1.35	10.1	1.75	13.2	10.2	76.5	13.25	0.00238
L21									
(repeat L12)	28	1.15	9.9	1.7	12.75	9.0	77.7	13.35	0.00230
L5									
(repeat L1)	28	1.1	8.7	3.25	13.05	8.45	66.7	24.9	0.00235
L31	28	0.95	7.9	4.45	13.3	7.2	59.4	33.4	0.00240
L27									
(repeat L12)	56	1.3	10.9	3.3	15.5	8.4	70.3	21.3	0.00280
L28									
(repeat L18)	56	0.8	9.4	4.2	14.4	5.6	65.3	29.2	0.00260
L32									
(repeat L28)	28	0.7	10.3	4.95	15.95	4.4	64.6	31.0	0.00287
L33									
(repeat L31)	28	0.9	9.35	6.0	16.25	5.5	57.6	36.9	0.00293
L34	28	0.85	9.1	6.8	16.75	5.1	54.3	40.6	0.00302

* Mixes L27, L28, L32, L33, L34 were made with $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ prepared by the method of Travers and Zahabi.

Table 8.—Invariant Point H:



H53	28	0.3	12.3	6.0	18.6	1.6	66.1	32.3	0.00335
H52	28	0.4	11.85	6.8	19.05	2.1	62.2	35.7	0.00343
H61									
(repeat H52)	28	0.25	12.4	7.05	19.7	1.3	62.9	35.8	0.00355
L22	28	0.5	11.0	6.4	17.9	2.8	61.5	35.7	0.00323
H64	7	0.1	11.8	8.7	20.6	0.5	57.3	42.2	0.00371
H65	28	0.2	11.2	8.2	19.6	1.0	57.2	41.8	0.00353
Mean value									
H53-H65	—	0.3	11.9	7.3	19.3	1.55	61.2	37.2	0.00348

Table 9.—Partial Cross-Section of the Quaternary System through the plane $\text{H}_2\text{O} - (\text{CaO})_s - \text{Al}_2(\text{SO}_4)_3$.

G4	7	3.35	6.35	3.6	13.3	25.2	47.7	27.1	0.00240
G9									
(repeat G4)	28	2.9	5.9	3.1	11.9	24.4	49.6	26.0	0.00215
I2	7	2.5	5.2	2.65	10.35	24.2	50.2	25.6	0.00187
I4	7	0.6	14.65	0.7	15.95	3.8	91.8	4.4	0.00288
G8	7	0.4	39.0	0.1	39.5	1.0	98.8	0.25	0.00712

TABLES V-X.—Continued.

No.	Time Shaken (Days).	G. mol. $\times 10^4$ per 1000 g. Solution.			Total g. mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(\text{CaSO}_4)_s$	Mol. % $(\text{CaO})_s$	Mol. % Al_2O_3	Mol. % Total Salts in Solution.
		$(\text{CaSO}_4)_s$	$(\text{CaO})_s$	Al_2O_3					

Table 10.—Boundary Curve MN :

 $\text{C}_2\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}-\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$. (Mixes C21-C34 and C36.)

Invariant Point N :

 $\text{C}_2\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}-\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}-\text{Al}_2\text{O}_3$ aq. (Mixes H54-H62.)

Invariant Point M :

 $\text{Ca}(\text{OH})_2-\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}-\text{C}_2\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ (Mixes C35, C37.)

C21	7	0.35	14.5	6.1	20.95	1.65	69.2	29.1	0.00378
C26									
(repeat C21)	28	0.35	14.15	4.95	19.45	1.8	72.8	25.5	0.00351
C30									
(repeat C23)	28	0.25	25.6	2.45	28.3	0.9	90.4	8.65	0.00511
C36									
(repeat C34)	28	0.2	36.7	0.75	37.65	0.55	97.5	2.0	0.00679
C35	7	0.1	63.7	0.5	64.3	0.15	99.0	0.8	0.01160
C37									
(repeat C35)	28	0.1	62.9	0.35	63.35	0.15	99.3	0.55	0.01143
H54	28	0.25	14.85	7.65	22.75	1.1	65.3	33.6	0.00410
H59	28	0.2	15.2	7.75	23.15	0.85	65.7	33.6	0.00418
H62	28	0.25	14.2	7.15	21.6	1.15	65.8	33.1	0.00389

The Jänecke projection of the curve on to the base of the pyramid is the curve EJ in Fig. 11a. The curve, within the range examined, lies practically within the section of the pyramid contained by the plane passing through the H_2O point and the line E'J' on the base. Its position in space is shown in Fig. 4 within the triangular section $\text{H}_2\text{O}-99$ per cent. $(\text{CaSO}_4)_s-96$ per cent. $\text{Al}_2(\text{SO}_4)_3$. The two points F31, F32 (Table III) actually fall almost in the plane owing to the deviation of the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio from 3 and are therefore shown in this diagram.

The Isothermal Invariant Point $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}-\text{Al}_2\text{O}_3$ aq.— $\text{C}_2\text{A} \cdot 3 \text{CaSO}_4-32 \text{H}_2\text{O}$. (E.)—The data, with the exception of the preparation of the initial mix, details of which are henceforth omitted in order to save space, are given in Table V. The appearance of the alumina gel phase differed from that along the boundary curve $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}-\text{Al}_2\text{O}_3$ aq. It now occurred as rounded grains, with index 1.53-1.54. In these and all subsequent mixes, the alumina gel was identified by its characteristic mode of occurrence as isotropic rounded or irregularly shaped material. No satisfactory staining by Keisermann's¹⁷ method with Patent Blue solution could be obtained.

The Boundary Curve Al_2O_3 aq.— $\text{C}_2\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$. (EH.)—Selected data are given in Table V. The projection of the curve on to the base of the pyramid is the curve EH in Fig. 11a. This departs only slightly from the straight line E'H' and can therefore be represented in space with reasonable accuracy in the plane section of the pyramid passing through the H_2O point and the line E'H'. It is shown in Fig. 5. It is seen that there is a rapid diminution in concentration of the equilibrium solution as the curve moves away from the isothermal invariant point E,

¹⁷ S. Keisermann, *Kolloid chem. Beih.*, 1909-10, 1, 423.

and that eventually the concentration increases again. Shortly after this increase in concentration occurs, the invariant point H, *i.e.* $\text{Al}_2\text{O}_3 \cdot \text{aq} - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ is reached.

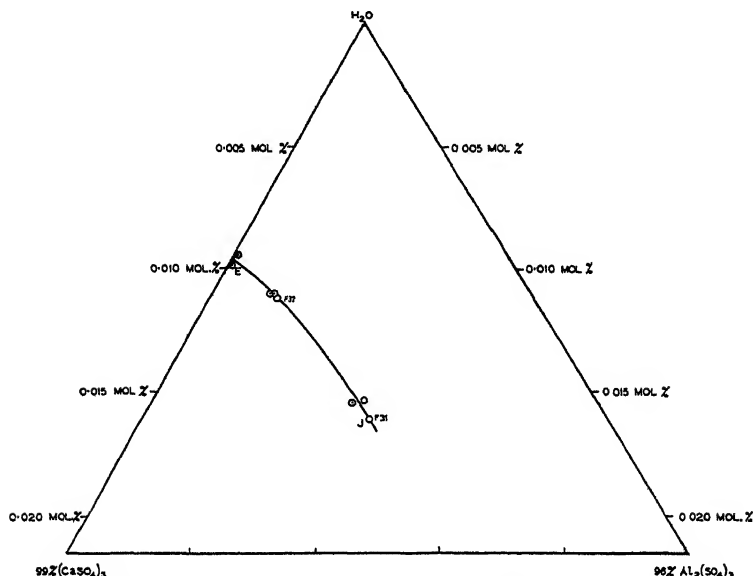
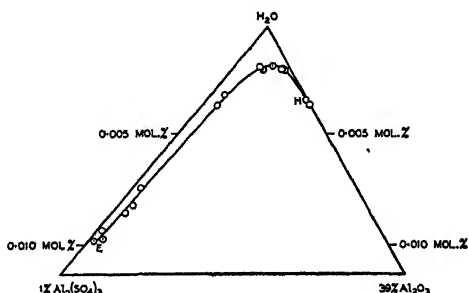


FIG. 4.—Quaternary system Boundary curve $\text{Al}_2\text{O}_3 \cdot \text{aq} - \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (EJ).

The portion of the curve near the invariant point E was determined starting from appropriate mixes of solutions of aluminium sulphate, calcium sulphate and lime. In order to ensure an adequate amount of alumina gel in the equilibrium mix, mixes from H29 onwards were prepared with alumina gel precipitated in the cold from aluminium sulphate and lime solutions. The gel, as prepared, contained a considerable proportion of aluminium sulphate. The alumina gel occurred in general as isotropic irregular mottled grains of varying size and of refractive index

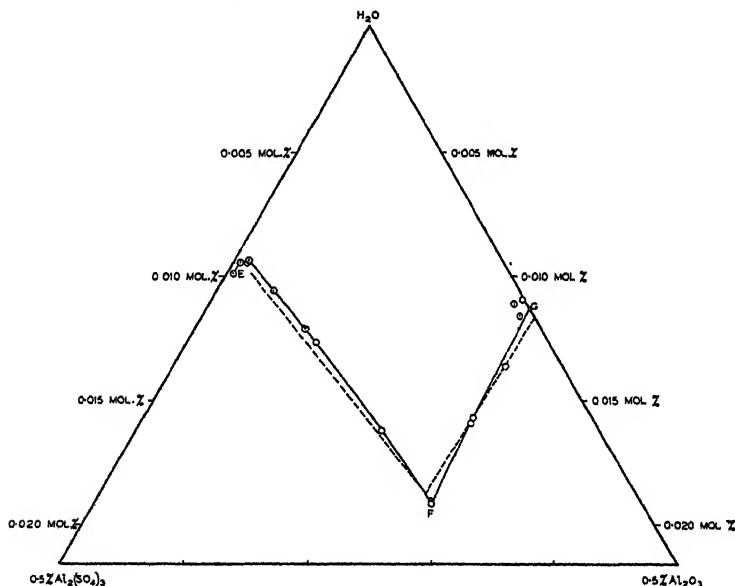
FIG. 5.—Quaternary system.
Boundary curve
 $\text{Al}_2\text{O}_3 \cdot \text{aq} - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ (EH).



approximately 1.525. The gel formed in mixes H15-H18 inclusive, that is, where directly precipitated from solution in the equilibrium mix, appeared as fairly clear cut rounded grains while in the remaining mixes, irregular mottled grains of varying size were formed. The needles of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ were in mixes H15-H18 of moderate size, fairly short and separate from the gel. In the remaining mixes where alumina gel was initially precipitated separately the needles were smaller, becoming very small in the solutions of high CaO and low CaSO_4 concentrations, and more or less embedded in the gel.

The Boundary Curve $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (EF.) The Boundary Curve $\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (FG.) The Invariant Point $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (F.)—Data are given in Table VI. The basal projections are the curves EF, FG of Fig. 11a. The position in space is shown in Fig. 6 within the triangular section of the pyramid $\text{H}_2\text{O}-0.5$ per cent. $\text{Al}_2(\text{SO}_4)_3-0.5$ per cent. Al_2O_3 . The dotted line shows the relative positions of the corresponding solubility curves for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ in the ternary system. The equilibrium mixes were prepared from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, and solutions of aluminium sulphate, lime and mixed lime-calcium sulphate.

The Invariant Point $\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}-\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ (G) was obtained by the addition of $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ to a mix designed to give a point on the $\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ boundary near to the



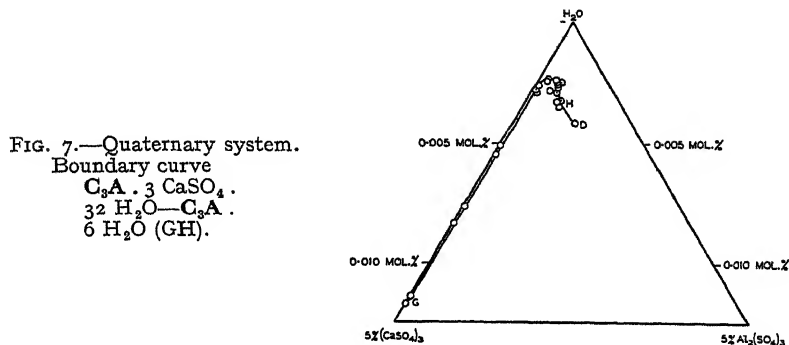
Boundary curves. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (EF).
 $\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (FG).
 Invariant Point. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}-\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. (F).

FIG. 6.—Quaternary system.

invariant point. Partial reaction of the $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ occurs to give $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. The data are given by L11 and L20 of Table VII.

The Boundary Curve $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}-\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ (GH) was obtained by means of mixes of 0.100 g. $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ and 125 ml. solution containing varying amounts and ratios of CaO and CaSO_4 . Most of the data were obtained using $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ prepared by autoclaving a mixture of C_3A and water. Several points were, however, also obtained using $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ prepared by the method of Travers and Zahabi. The fine-grained material prepared by the latter method gave rather higher contents of CaO and Al_2O_3 in solution than the relatively coarse-grained material prepared by autoclaving. Data are given in Table VII. The projection of the curve on to the base of the pyramid is the curve GH in Fig. 11a. Owing to its curvature it is possible to render the spacial position only approximately within the plane section of the pyramid $\text{H}_2\text{O}-5$ per cent. $(\text{CaSO}_4)_3-5$ per cent. $\text{Al}_2(\text{SO}_4)_3$. It is shown in Fig. 7.

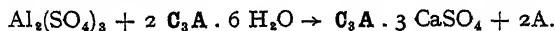
The position of the boundary curve HD, *i.e.* $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O} - \text{Al}_2\text{O}_3$ aq. is also shown approximately in this figure.



The Invariant Point $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 6 \text{H}_2\text{O} - \text{Al}_2\text{O}_3$ aq. (H.) may theoretically be attained in several ways:—

- (i) Al_2O_3 gel + $\text{Al}_2(\text{SO}_4)_3$ + CaO + $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.
- (ii) Al_2O_3 gel + CaSO_4 + CaO + $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.
- (iii) Al_2O_3 gel + $\text{Al}_2(\text{SO}_4)_3$ + $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.
- (iv) Al_2O_3 gel + CaSO_4 + $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.
- (v) $\text{Al}_2(\text{SO}_4)_3$ + $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.
- (vi) CaSO_4 + $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.

The mix represented by (i), as used in the investigation, consisted of alumina gel containing a proportion of $\text{Al}_2(\text{SO}_4)_3$, solutions of $\text{Al}_2(\text{SO}_4)_3$ and CaO , and $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$. It involves reaction of $\text{Al}_2(\text{SO}_4)_3$ with CaO to form $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$. If less CaO is present in the solution added than is required for this formation and for the equilibrium concentration, some decomposition of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ must occur. An example of this type of mix is given by H53 of Table VIII. If excess CaO is present, theoretically this should combine with some of the free alumina, and $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ should be formed. Owing to the difficulties inherent in the last-named method of approach in this system it cannot be conveniently employed to determine the invariant point. The mix represented by (ii) is essentially similar to (i) except that it may involve re-solution of some of the Al_2O_3 gel. It has not been used. Mixes (iii) and (iv) are similar to (i) and (ii) respectively except that no CaO is used. They involve reaction of $\text{Al}_2(\text{SO}_4)_3$ and CaSO_4 respectively with $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ to give $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$. Mixes of type (iii) are given by H52, H61 and L22 of Table VIII. Mix (iv) has not been used, but a combination of (iii) and (iv) is represented by mixes H64 and H65 of Table VIII. Mix (v) should lead to the formation of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ and Al_2O_3 gel according to the reaction:—



Thus with excess $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$, the invariant point should be obtained. Mix (vi) should also lead to formation of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$, and further slight decomposition of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ should theoretically occur, with deposition of alumina. In both cases (v) and (vi) anomalous results have been obtained which will be discussed later.

The analytical data show a moderate spread, apparently dependent on the composition of the initial mix. It is probable that the differences shown would tend to disappear with increased periods of shaking. The mean of the six mixes gives for the invariant point the concentration in g. per 1000 g. solution $\text{CaO} = 0.200$, $\text{Al}_2\text{O}_3 = 0.074$, $\text{SO}_3 = 0.007$, or in g.-mols. $\times 10^4$ per 1000 g. solution: $\text{CaO} = 35.7$, $\text{Al}_2\text{O}_3 = 7.3$, $\text{CaSO}_4 = 0.9$.

Partial Cross-section of the Quaternary System through the Plane $\text{H}_2\text{O}-(\text{CaO})_3-\text{Al}_2(\text{SO}_4)_3$.—Data are given in Table IX for mixes of lime and aluminium sulphate solutions (G mixes), and lime solution with 0.100 g. $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ (I mixes). It is to be noted that the projected points in Fig. 11a all fall on the diagonal $(\text{CaO})_3-\text{Al}_2(\text{SO}_4)_3$. The special position is given in Fig. 8. The significance of these data is discussed below in considering the complete system.

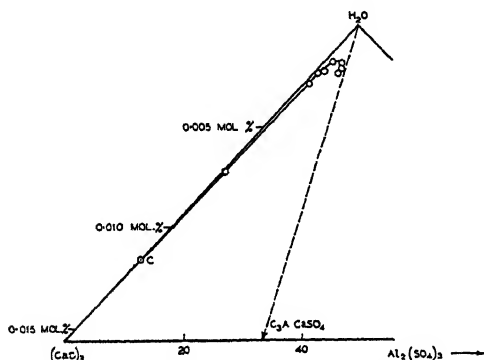
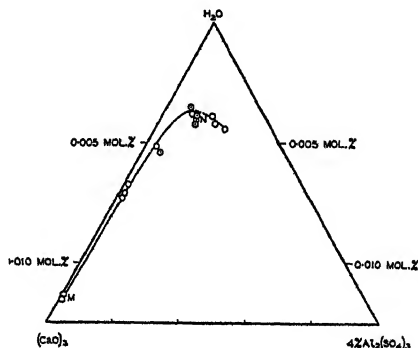


FIG. 8.—Quaternary system. Cross section through plane $\text{H}_2\text{O}-(\text{CaO})_3-\text{Al}_2(\text{SO}_4)_3$.

The Boundary Curve $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}-\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$. (MN.)—Data are given in Table X. All data are plotted in Figs. 9 and 11b. They were obtained by shaking 0.100 g. of the crushed balls of $\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$ (see preparation) with lime-calcium sulphate solutions of various concentrations, so that partial conversion to $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ was caused. With increasing concentrations of lime in solution it was found necessary to increase the concentration of calcium sulphate before conversion was effected.

FIG. 9.—Quaternary system. Boundary curve $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}-\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$ (MN).



The Quaternary Invariant Point $\text{Ca}(\text{OH})_2-\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}-\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ (M) was obtained with mixes C35 and C37 of Table X.

The Quaternary Invariant Point $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}-\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}-\text{Al}_2\text{O}_3$ aq. (N) may theoretically be attained in several ways as described for the corresponding invariant point with $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$, substituting $\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$ for $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.

As in the case of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ mixes (ii) and (iv) have not been employed.

The mix represented by (i) was prepared similarly to that used for $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$. As before, if less CaO is present in the solution added than is required for this formation and for the equilibrium concentration, some decomposition of $\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$ must occur. If excess CaO is present then to obtain the invariant point, the excess CaO would have to combine

with some of the free alumina and form $C_2A \cdot 8 H_2O$. Owing to the metastable nature of this phase its formation is doubtful, and in fact mixes prepared under such conditions showed increased concentrations of CaO and Al_2O_3 in solution above that corresponding to the true equilibrium point. Mixes corresponding to the first method of approach involving some decomposition of added $C_2A \cdot 8 H_2O$ are given in Table X. The mean of the three 28-day mixes quoted, which are in good agreement, gives for the invariant point the concentrations in g. per 1000 g. solution: $CaO = 0.251$, $Al_2O_3 = 0.077$, $SO_3 = 0.006$; or in g. mol. $\times 10^4$ per 1000 g. solution: $CaO = 43.25$, $Al_2O_3 = 7.50$, $CaSO_4 = 0.75$. Mixes of types (v) and (vi) gave anomalous results and are discussed later.

Removal of Calcium Sulphate from Solution by $C_2A \cdot 8 H_2O$.—Attempts were made to get partial conversion of $C_2A \cdot 8 H_2O$ to $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ by shaking for periods of 7 and 28 days 0.100 g. of crushed $C_2A \cdot 8 H_2O$ with 125 ml. of calcium sulphate solutions of various

TABLE XI.—REMOVAL OF CALCIUM SULPHATE FROM SOLUTION BY $C_2A \cdot 8 H_2O$.

No.	Days Shaken	Initial Solution (g. per Litre.)		Equilibrium Solution g. per 1000 g. Solution.			g. $CaSO_4$ removed per 1000 g. Solution.	Solid Phases.	Calculated Molar Ratio in Solid Phase. $CaO : Al_2O_3 : CaSO_4$.
		$CaSO_4$.	CaO .	$CaSO_4$.	CaO .	Al_2O_3 .			
B1	7	0.100	—	0.0645	0.150	0.162	0.0355	" $C_2A \cdot 8 H_2O$ "	2 : 0.58 : 0.26
B7	7	0.126	—	0.090	0.162	0.162	0.036	" "	2 : 0.54 : 0.29
B11, 12, 13	7	0.176- 0.187	—	—	—	—	—	" "	
B15	7	0.195	—	0.078	0.138	0.150	—	" $C_2A \cdot 8 H_2O$ " $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$	
B5a	7	0.203	—	—	—	—	—	" $C_2A \cdot 8 H_2O$ "	
B6a	28	0.152	—	0.1095	0.159	0.155	0.0425	" $C_2A \cdot 8 H_2O$ "	2 : 0.7 : 0.26
B8	28	0.177	—	0.141	0.153	0.153	0.036	" "	2 : 0.69 : 0.26
B16	28	0.180	—	—	—	—	—	" "	
B14	28	0.182	—	—	—	—	—	" "	
B10	28	0.187	—	—	—	—	—	$C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$	
C11a	28	0.150	0.100	0.109	0.160	0.109	0.041	" $C_2A \cdot 8 H_2O$ "	2 : 0.6 : 0.17
C38	7	0.150	0.500	0.0045	0.460	0.0445	0.1455	" "	2 : 0.56 : 0.35
C39	7	0.150	0.750	0.0025	0.618	0.012	0.1475	" "	2 : 0.52 : 0.28
C32	7	0.200	1.07	0.005	1.051	0.0035	0.195	" "	2 : 0.73 : 0.49

concentrations. The results are given in Table XI. It was found that sulphate was removed from solution without any apparent change in the $C_2A \cdot 8 H_2O$ as shown by microscopic examination other than a slight lowering of refractive index. Within the limits of experimental error the amount removed was constant throughout a range of concentrations. It was found that formation of $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ occurred quite sharply when the concentration exceeded a certain value, and in the case of 28-day mixes complete conversion then occurred. Only in the case of one 7-day mix, B15, was partial conversion found. The composition of the solid phase consisting of apparently unchanged $C_2A \cdot 8 H_2O$, calculated from the initial and final solution concentrations and the known amount of $C_2A \cdot 8 H_2O$ used, was $Ca : Al_2O_3 : CaSO_4 = 2 : 0.6—0.7 : 0.26$. The mixes B1a, B7, B6a, B8 of Table XI form a series of solutions in metastable equilibrium with this solid phase. They are plotted in Fig. 10. Once formation of $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ commenced, there was a sharp fall in the concentrations of lime and calcium sulphate in solution and to a lesser extent of alumina to the values given for B15. With the introduction of added lime into the mix, there appears at first to be no change

in the absolute amount of calcium sulphate removed, as shown by C11a, though the molar proportion is reduced. The remaining mixes C38, C39 and C32 indicate, however, that further additions of lime increases the amount removed considerably. This point has not been pursued, but the limited data obtained suggest that above certain lime concentrations, calcium sulphate may be continuously removed as the concentration of this salt is increased, until finally formation of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ takes place. It is at any rate clear that along the $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$ boundary we are not dealing with a pure $\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$, but rather with a solid solution of $\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$, lime and calcium sulphate. In this connection it is of interest to note that Assarsson has reported a penta-calcium aluminate hydrate $\text{C}_5\text{A} \cdot 32 \text{H}_2\text{O}$, which usually contained a trace of SO_3 .

Anomalous Results.—Before proceeding to a discussion of the quaternary system as a whole, it is desirable to consider some apparent anomalies obtained with certain types of mixes. In order to avoid confusion, such results are plotted separately (in projection) in Fig. 10. The actual data are omitted. Mixes K3 and K5 are of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ and aluminium sulphate solution, and should lead to the invariant point

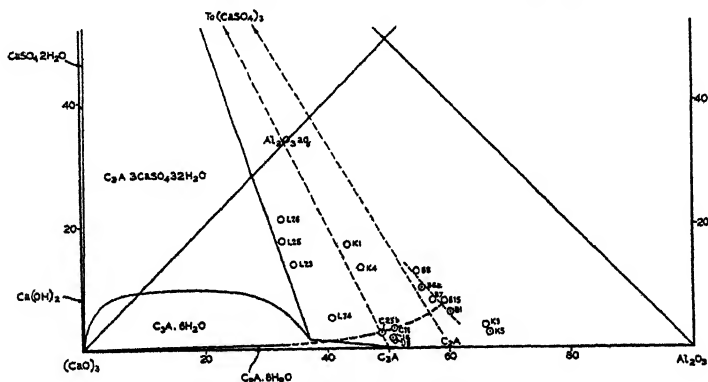
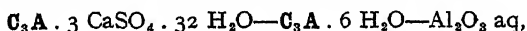
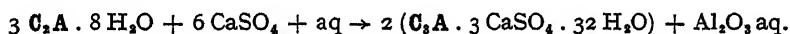


FIG. 10.—Anomalous results.

as previously indicated. Actually no Al_2O_3 aq separated from solution, the only solid phases being $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ and $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$. It seems necessary to conclude that the Al_2O_3 is retained in colloidal solution, and that equilibrium (from the phase-rule standpoint) is therefore not reached. Mixes K1 and K4 are of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ and calcium sulphate solution. As previously indicated, the same invariant point should theoretically be attained. Al_2O_3 aq can, however, not here be formed in the course of formation of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$, but should be produced as a result of incongruent solution of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$. The amount to be expected is small. No Al_2O_3 aq was detected microscopically, the solid phases found being $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ and $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ for K1 and $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ only for K4, using half the CaSO_4 concentration of K1. The solution compositions also point to non-formation of Al_2O_3 aq since they lie approximately on the line joining the C_3A composition point to the $(\text{CaSO}_4)_2$ corner. This is to be expected from congruent solution of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ and a simple formation of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ without deposition of alumina. The calcium sulphate concentration of the solution is much higher than at the invariant point. This behaviour suggests that some inhibiting factor plays a part in interfering with the course of the reaction. It is a possibility that this factor may

be the formation of a thin coating of Al_2O_3 aq round the grains of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$. Mixes L23, L25 and L26 are repeats for 7, 28 and 56 days' shaking of a mix consisting of 0.100 g. $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ and 125 ml. of solution containing calcium sulphate (0.162 g. CaSO_4 per litre) and lime (0.050 g. CaO per litre). The found position of the invariant point indicates that such a mix should give the invariant point with Al_2O_3 aq. $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ formation in approximately equal amount occurred with L23 and L25, but not with L26. No Al_2O_3 aq was found in the solid phase by microscopic examination, and the calcium sulphate concentration is again much higher than what appears to be the true equilibrium value as found from numerous other data along the boundary curve or at the invariant point. Mix L34 similar to those above, but using the much finer grained $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ prepared by the method of Travers and Zahabi, gave on the other hand a much lower value for the calcium sulphate concentration. This lends support to the idea of an inhibiting film formed on the surface of the grains, since with the larger surface area provided in the second case, the reaction can proceed further towards equilibrium before being brought to a stop. Similar types of mixes with larger amounts of lime (0.075 g. CaO per litre and above) were normal in behaviour. In these, incongruent solution of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ with deposition of alumina is not to be expected.

Mixes similar to K3 and K5, but using $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ in place of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$, are illustrated by mixes J6 and J8. A similar behaviour is shown. The behaviour of $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ with a solution of calcium sulphate only has been previously discussed. It is clear from the position of the invariant point that theoretically such mixes or those containing only small amounts of lime should give this point, according to the equation:—



Thus Mix B15 containing calcium sulphate only, and mixes C11 and C25b containing respectively 0.150 g. and 0.175 g. CaSO_4 per litre and in addition 0.100 g. CaO per litre, should give this point. Actually only " $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ " and $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ were present as solid phases. If no interfering factor arises as has been discussed above for similar mixes involving $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$, the resulting data represent a metastable prolongation of the metastable " $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ "— $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ boundary. This is shown by the dotted line in Figs. 10 and 11b.

The Space Figure and the Basal Projection.—A space model has been constructed and photographs are given in the Plate. Equilibria involving $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ are not included. The boundary curves and invariant points shown are as follows:—

(a) Ternary System H_2O — $(\text{CaO})_3$ — Al_2O_3 .

H_2O —D = Al_2O_3 aq.

D = Al_2O_3 aq— $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.

DC = $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$.*

C = Solubility of crystalline $\text{Ca}(\text{OH})_2$ in water.

(b) Ternary System H_2O — $(\text{CaO})_3$ — $(\text{CaSO}_4)_3$.

CB = $\text{Ca}(\text{OH})_2$ (crystalline).

B = Crystalline $\text{Ca}(\text{OH})_2$ — $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

BA = $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

A = Solubility of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ in water.

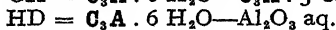
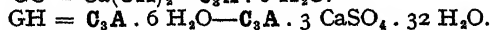
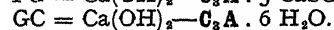
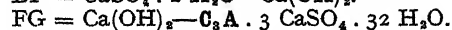
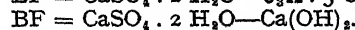
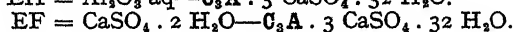
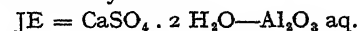
(c) Ternary System H_2O — $(\text{CaSO}_4)_3$ — $\text{Al}_2(\text{SO}_4)_3$.

AI = $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

* It is possible that C_4A aq may appear as a stable phase at the upper limit of lime solubility.

(d) Quaternary System.

(i) Boundary curves.



(ii) Invariant points.

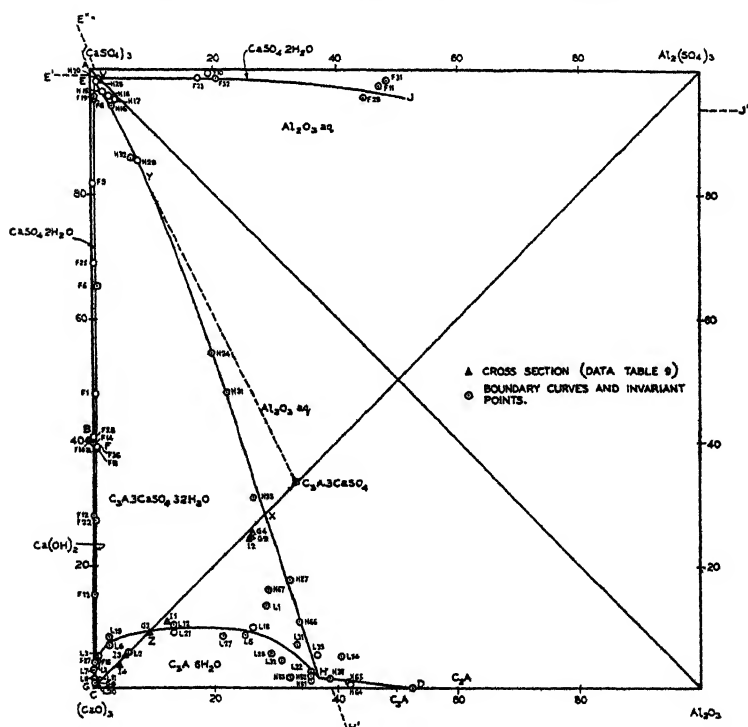
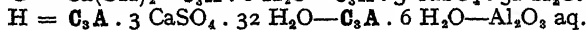
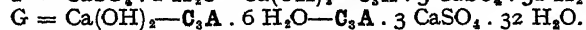
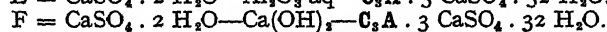
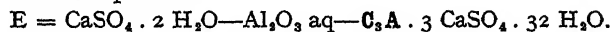
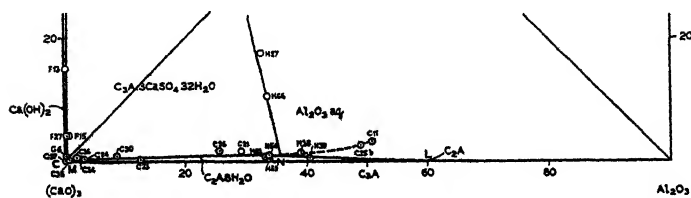


FIG. 11a.—Quaternary system. Projection on base of pyramid.

FIG. 11b.—Quaternary system. Projection on base of pyramid. Portion showing $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ equilibria.

The projection on to the base of the pyramid by means of lines drawn through the H_2O point is shown in Fig. 11a. Fig. 11b shows the modification introduced by the substitution of $\text{C}_3\text{A} \cdot 8 \text{H}_2\text{O}$ for $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$. Invariant point compositions are collected together in Table XII.

TABLE XII.—INVARIANT POINT COMPOSITIONS.

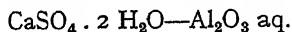
	Invariant Point.	g. Mol. $\times 10^4$ per 1000 g. Solution.			Total g.-Mol. $\times 10^4$ per 1000 g. Solution.	Mol. % $(\text{CaSO}_4)_s$.	Mol. % $(\text{CaO})_s$.	Mol. % Al_2O_3 .	Mol. % Total Salts in Solution.
		$(\text{CaSO}_4)_s$.	$(\text{CaO})_s$.	Al_2O_3 .					
E	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} - \text{Al}_2\text{O}_3 \text{ aq} - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$	52.5	0.45	0.6	53.6	98.1	0.85	1.15	0.00966
F	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} - \text{Ca}(\text{OH})_2 - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$	41.1	64.1	0.6	105.8	38.8	60.6	0.6	0.01907
G	$\text{Ca}(\text{OH})_2 - \text{C}_3\text{A} \cdot 6 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$	0.6	63.3	0.1	64.0	0.95	99.0	0.15	0.01153
H	$\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 6 \text{H}_2\text{O} - \text{Al}_2\text{O}_3 \text{ aq}$	0.3	11.9	7.3	19.3	1.55	61.2	37.2	0.00348
M	$\text{Ca}(\text{OH})_2 - \text{C}_3\text{A} \cdot 8 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$	0.1	63.3	0.4	63.8	0.15	99.15	0.7	0.01152
N	$\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O} - \text{C}_3\text{A} \cdot 8 \text{H}_2\text{O} - \text{Al}_2\text{O}_3 \text{ aq}$	0.25	14.75	7.5	22.5	1.1	65.6	33.3	0.00406

Discussion.

It has been pointed out in the introduction that the fundamental stable quaternary system involves equilibria with crystalline $\text{Ca}(\text{OH})_2$ and crystalline $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$. Equilibria with alumina gel are therefore strictly to be regarded as metastable equilibria only. The changing appearance of the gel suggests that at any rate along the $\text{Al}_2\text{O}_3 \text{ aq} - \text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ boundary we are not dealing with a pure phase, but one which probably contains both CaO and SO_3 possibly in increasing amount as the lime concentration in solution increases. The solid phases occurring in the quaternary system at 25°C . as at present worked out consist therefore of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ as the only quaternary compound, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, crystalline $\text{Ca}(\text{OH})_2$, $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$, " $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ " (metastable, and containing lime and calcium sulphate in solid solution) and " $\text{Al}_2\text{O}_3 \text{ aq}$ " (probably in general containing CaO and SO_3).

Referring to Fig. 11, the following conclusions are to be drawn:—

(i) The pair $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \text{ aq}$ co-exist at 25°C . and the system $\text{H}_2\text{O} - \text{Al}_2\text{O}_3 - \text{CaSO}_4$ is a ternary one. The point V, where the boundary curve $\text{Al}_2\text{O}_3 \text{ aq} - \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ cuts the diagonal $(\text{CaSO}_4)_s - \text{Al}_2\text{O}_3$ corresponds to the ternary invariant point



(ii) The quaternary compound $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ is incongruently soluble in water and in dilute solutions of both lime and calcium sulphate decomposing to a slight extent to give $\text{Al}_2\text{O}_3 \text{ aq}$ as a second solid phase. The minimum concentration of lime water in which it becomes congruently soluble is given by the point X and of calcium sulphate

by the point Y. The molecular percentages of the components of the salt mixture at these points are respectively:—

$$X = 28.0\% (\text{CaSO}_4)_3, 44.0\% (\text{CaO})_3, 28.0\% \text{Al}_2\text{O}_3,$$

$$Y = 80\% (\text{CaSO}_4)_3, 10\% (\text{CaO})_3, 10\% \text{Al}_2\text{O}_3,$$

and the molecular percentages of total salts in solution (by interpolation on the boundary curve $\text{Al}_2\text{O}_3 \text{ aq}-\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$) are $X = 0.0018\%$, $Y = 0.00285\%$. The respective concentrations in g. per 1000 g. solution of CaO and CaSO_4 other than as $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ are $X = 0.027 \text{ g. CaO}$, $Y = 0.45 \text{ g. CaSO}_4$. The $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ remains congruently soluble in calcium sulphate solutions of all concentrations greater than 0.45 g. CaSO_4 per 1000 g. solution up to saturation point, but Fig. 11 indicates that in lime solutions the compound again becomes incongruently soluble with respect to the stable phase $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ at point Z. At this point, from interpolation on the boundary curve $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}-\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$, the molecular

TABLE XIII.—SOLUBILITY OF $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ IN LIME SOLUTIONS.

Concentration per 1000 g. Solution.			
CaO .		$\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$.	
g.-mols. $\times 10^4$.	g.	g.-mols. $\times 10^4$.	g.
6.5	0.0365	3.0	0.375
10.0	0.056	2.05	0.255
20.0	0.112	1.3	0.165
30.0	0.168	0.9	0.115
40.0	0.224	0.65	0.080
120.0	0.67	0.25	0.030

percentage of total salts in solution is 0.00235 , while from interpolation on the cross-section along the diagonal $(\text{CaO})_3-\text{Al}_2(\text{SO}_4)_3$ it is 0.0020 , mean = 0.0022 . The percentages of the components of the salt mixture are $9.5\% (\text{CaSO}_4)_3$, $81\% (\text{CaO})_3$, $9.5\% \text{Al}_2\text{O}_3$, and the corresponding concentration of lime other than as $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ is 0.15 g. CaO per 100 g. solution . Thus $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ treated with lime solutions of concentrations greater than this value should theoretically undergo decomposition with production of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ as a second solid phase, and dissolution of calcium sulphate until the concentration of the solution corresponds to some point on the boundary curve $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}-\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ between Z and G. In practice it has been found that such mixes do not give $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ after 7 days' shaking. As will be evident from Table IX and Fig. 11a, the resulting solutions represent congruent solutions of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ in lime solutions up to the highest lime concentration used. The amount of decomposition which is to be expected is, however, quite small. Thus Mix 14 (Table IX) using a lime concentration of 0.25 g. CaO per litre should yield about $0.002 \text{ g. C}_3\text{A} \cdot 6 \text{H}_2\text{O}$, derived from 0.006 g. of the $0.100 \text{ g. C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ used. In view of the difficulties met with in the ternary system $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}$ as regards crystallisation of $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ it is not surprising that within the short period of 7 days $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ has not been formed. From the data of Fig. 8, the solubility of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ in lime solutions may be derived. Above a lime concentration amounting to 0.15 g. CaO per 1000 g. solution the solution is, of course, metastable. Table XIII gives interpolated data.

(iii) Consideration of Fig. 11 throws light on the curves previously

obtained by Lafuma,¹⁸ Foret,⁵ and the present writer,⁶ expressing the concentrations of solutions obtained by shaking $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ with lime and calcium sulphate solutions. The data previously obtained fall along the boundary curve $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O} - \text{Al}_2\text{O}_3$ aq and the section of the $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ field along the diagonal $(\text{CaO})_3 - \text{Al}_2(\text{SO}_4)_3$ consisting of congruent solutions of $\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$ in lime solutions together with its metastable prolongation into the $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ field.

The Calcium Sulphoaluminate in Hydrated Portland Cement.

It is fairly generally agreed that during the setting of Portland cement the gypsum added as retarder forms a calcium sulphoaluminate, though Roller¹⁹ considers that reaction results mainly in the formation of $\text{Ca}(\text{OH})_2$ and alkali sulphate. Koyanagi²⁰ reports that only the high sulphate form exists in hydrated Portland cement. Forsén²¹ has recently expressed the view that it is probably the low sulphate form, $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12 \text{H}_2\text{O}$ which is produced. On shaking " C_2A melt" and C_3A with saturated lime-gypsum solutions for 3 months, the solid residues gave analyses suggesting the low sulphate form, though it is pointed out that it was not identified microscopically and embedded C_3A grains were still present. In the present work, using $\text{C}_3\text{A} \cdot 6 \text{H}_2\text{O}$ and $\text{C}_2\text{A} \cdot 8 \text{H}_2\text{O}$ only the high sulphate form, identified microscopically, has been obtained in lime-calcium sulphate solutions containing up to 1.075 g. CaO per 1000 g. solution (saturated with respect to crystalline $\text{Ca}(\text{OH})_2$) and 1.055 g. CaO per 1000 g. solution respectively. The form of lime used by Forsén appears to be that obtained by ignition of the hydroxide at 600° C. and yields a higher CaO concentration than that obtained with crystalline $\text{Ca}(\text{OH})_2$. Further evidence for low sulphate formation was obtained by Forsén on storing in moist air four set cements containing 10 per cent. of added gypsum. After 28 days combined SO_3 calculated as a percentage of the Al_2O_3 content amounted to 84, 81, 79 and 71 per cent. respectively, compared with 79 % required for conversion of Al_2O_3 to low sulphate. The fairly close agreement between found and theoretical values is suggestive, but depends, however, on the assumption that all the alumina has combined to give a sulphoaluminate. The results of the present work show that within the quaternary system examined, using crystalline $\text{Ca}(\text{OH})_2$ and alumina gel, up to the limits of CaO concentration imposed by crystalline $\text{Ca}(\text{OH})_2$ as solid phase, $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12 \text{H}_2\text{O}$ is not formed at 25° C. The writer⁶ has indicated elsewhere that the stability conditions for this compound involve high CaO and low CaSO_4 concentration and high temperature. In so far as the CaO concentration in a set cement exceeds that given by crystalline $\text{Ca}(\text{OH})_2$, the CaO value may rise sufficiently high to stabilise the low sulphate form. Thus Forsén gives values for a supersaturated lime solution from an alkali-free cement, without gypsum, water-cement ratio = 0.60, rising to 1.7 g. CaO per litre in 5 min. and then falling to a value of 1.5 g. CaO per litre. Normally, however, one has to deal with cements containing alkali,

¹⁸ H. Lafuma, *The calcium aluminates and their compounds with calcium chloride and calcium sulphate*, Paris, 1932 (Librairie, Vaibert), pp. 67.

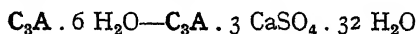
¹⁹ P. S. Roller, *J. Ind. Eng. Chem.*, 1934, 26, 669.

²⁰ K. Koyanagi, *Zement*, 1931, 20, 1016.

²¹ L. Forsén, *Symp. Chem. Cements*, Stockholm, 1938, 298.

and Roller has shown that the solution which is formed in such cements during setting consists mainly of alkali sulphate and hydroxide. The CaO concentration may be thus much reduced. The effect of alkalis on the formation of sulphoaluminates is not known except for an observation by Lerch, Ashton and Bogue² that both high and low sulphate forms of calcium sulphoaluminate are unchanged when in contact with a 3 per cent. NaOH solution. Work is being pursued by the writer to determine how alkalis may modify the equilibria determined for the quaternary system. A possible factor in assisting formation of the low sulphate form is that of heat evolution during hydration. In this connection the work of Schl pfer²² is of interest. This author has reported the results of mixing water with C_3A and increasing additions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. With 5 % and 10 % of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the formation of circumferential zones of $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ around the C_3A grains was found, while 20 % and 40 % of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ gave the high sulphate form. It seems possible that the formation of the low sulphate form may result from local rise of temperature at the surface of the C_3A grains.

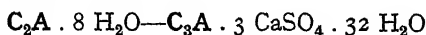
The Attack of Calcium Sulphate Waters on Concrete.—The data which have been obtained are of special interest in relation to attack on concrete by water containing dissolved calcium sulphate. It is generally held that disintegration under such conditions is the direct result of the formation of the high sulphate form of calcium sulphoaluminate. It is of interest to consider what is the limiting concentration of calcium sulphate below which no formation of $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ and therefore no disintegration can occur. The compounds with which we have to deal in this connection are essentially the stable cubic $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ and the metastable hexagonal plate forms of the calcium aluminate hydrates. Cubic $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ is not a normal constituent of either a Portland or aluminous cement mortar or concrete, for although it is the stable phase up to a concentration of lime saturated with respect to crystalline lime (see footnote, p. 1503) though not with respect to finely divided or amorphous lime, it seems that the metastable compounds are formed preferably and persist indefinitely. It is usually considered that these compounds will be $\text{C}_3\text{A} \cdot 11-12\text{H}_2\text{O}$ or $\text{C}_4\text{A} \cdot 12-13\text{H}_2\text{O}$, though the influence of alkali in modifying the equilibria is not yet worked out. Theoretically, unless the compound $\text{C}_4\text{A} \cdot 12-13\text{H}_2\text{O}$ is stable in saturated lime solution, there is a tendency on ageing for the metastable compounds to change over to the cubic $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$. Although this change may not occur in practice it is of fundamental value to consider what would be the behaviour of this compound when exposed, as a constituent of such a concrete, to calcium sulphate waters. This behaviour is given by the boundary curve



in the quaternary system. Thus Table VII gives for various concentrations of lime and alumina in solution the concentrations of calcium sulphate below which no formation of $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ can occur. For example, where the concentration of lime can be maintained at 1.05 g. CaO per litre, a concentration of greater than 0.019 g. CaSO_4 per litre will permit of formation of $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. It seems likely that corresponding equilibria with the metastable hexagonal

²² P. Schl pfer, *Symp. Chem. Cementis*, Stockholm, 1938, 270.

$C_3A \cdot 11-12 H_2O$ would show rather lower values for the calcium sulphate required for conversion to $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$. This would apply all the more to $C_4A \cdot 12-13 H_2O$ since formation of $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ involves an increase in the lime concentration of the solution. In the case of $C_2A \cdot 8 H_2O$ we are concerned with the data obtained for the boundary curve



(Table X). There is, however, a difference resulting from the fact that $C_2A \cdot 8 H_2O$ takes up calcium sulphate from solution before conversion to $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ occurs. The amount so taken up appears to depend on the content of lime in solution. Table XI shows that in the absence of lime, conversion may occur after initial absorption of calcium sulphate at a minimum content of 0.145 g. $CaSO_4$ per litre. In the presence of an adequate amount of lime, Table XI shows that calcium sulphate may be taken up from solution and conversion eventually occur at concentrations down to the very low values of Table X, for example, in saturated lime solution at 0.004 g. $CaSO_4$ per litre.

The equilibria with $C_2A \cdot 8 H_2O$ are of special interest in connection with the considerable resistance shown by aluminous cement to sulphate attack. The hydration products of aluminous cement are not known with certainty, but it appears that $C_2A \cdot 8 H_2O$ and alumina gel tend to separate at room temperature from the initial reaction product (probably a mono-calcium aluminate hydrate (Assarsson²³), while at higher temperatures further decomposition of $C_2A \cdot 8 H_2O$ to cubic $C_3A \cdot 6 H_2O$ and alumina gel occurs. The present work shows that in so far as $C_2A \cdot 8 H_2O$ may be exposed to the action of calcium sulphate, formation of $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ must occur. Protection of $C_2A \cdot 8 H_2O$ may, however, arise in at least two ways. In the first place, the alumina gel originally precipitated in the hydrating cement may form a protective coating. In this connection, as has been seen, alumina gel does not interact with calcium sulphate in the absence of lime. In the second place, the production of $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ from $C_2A \cdot 8 H_2O$ results also in the release of alumina into solution, and unless conditions are such that the alumina is removed as fast as it is formed, the concentration will eventually rise to such a point that gel is precipitated.

Summary.

Calcium sulphoaluminates arise during the setting of Portland cement and by the action of sulphate waters on concrete. In order to determine the precise conditions of their formation, a study of the quaternary system $CaO-Al_2O_3-CaSO_4-H_2O$ has been undertaken. The method adopted is to consider the system as formed by reciprocal salt pairs. The present work at 25° C. includes crystalline $Ca(OH)_2$ and the gel form of hydrated alumina as solid phases. That portion of the system of particular interest in cement chemistry has been worked out, and a space model constructed. The following main conclusions are made:—

Only the high sulphate form of calcium sulphoaluminate occurs. This compound is incongruently soluble in water and in dilute solutions of both lime and calcium sulphate. Above a certain concentration of calcium sulphate it is stable, but in lime solutions it is congruently soluble only within a limited range of concentrations. The curves previously reported

²³ G. Assarsson, *Symp. Chem. Cements*, Stockholm, 1938, 441.

by various authors expressing the concentrations of solutions obtained by shaking $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ CaSO}_4 \cdot 32 \text{ H}_2\text{O}$ with lime and calcium sulphate solutions are shown to consist in part of the boundary curve $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ CaSO}_4 \cdot 32 \text{ H}_2\text{O} - \text{Al}_2\text{O}_3 \text{ aq}$ and in part of a section of the $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ CaSO}_4 \cdot 32 \text{ H}_2\text{O}$ field.

The nature of the calcium sulphotoaluminate formed in hydrated Portland cement is discussed, and the application of the results to the attack of calcium sulphate waters on concrete considered.

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ON THIN PROTEIN MEMBRANES.

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It is possible to deposit protein monolayers on "frames" consisting of fine meshed metallic gauzes or stretched silk by the dipping technique of Blodgett.¹ The protein used was egg albumen spread from a powder at an air-distilled water interface using triolein or castor oil as pistons. Deposition takes place both on dipping the "frame" through the monolayer and on withdrawal, provided the film is dried after each withdrawal. The gauzes were of copper of 30μ mesh made of wire 10μ diameter, which was then rolled out till the gauze occupied about twice its original area; the silk frame was washed initially in petrol ether to free from grease.

A similar process was watched on a loop of 0.2 mm. diameter of fine glass thread. The protein was put on at high compression as a very elastic film so that as it dried and shrank it was able to stretch and put a tension on the glass loop. The protein as it dries stretches and ultimately tears and subsides so as to span regions of greater curvature of the irregular loop. After two or three dippings a considerable fraction of the loop was covered with dried albumen and the tension began to deform the loop. Subsequent depositions leave a smaller and smaller area uncovered by protein until after some 50 or 60 dippings the whole loop in its deformed state is spanned by protein. Some of the sheets have tears (or cracks), but these have presumably become covered up by subsequent depositions. Thus the loop eventually gets considerably deformed and is completely spanned by protein which is thicker near the glass at the periphery: sometimes the first few sheets after tearing wind up round the fibre instead of just collapsing on to it, but this also leads to thicker protein near the glass. Tears in individual layers are scattered sporadically through the micromembrane, but in general get completely covered by subsequent depositions. The resulting micromembranes were stable for months when kept in dry air.

Presumably a similar type of process takes place with the metal gauze. If the wires of the latter are thick the protein layers deposited on each side occlude a bigger volume of water than if they are thin. With the thicker wires the water takes longer to evaporate away and there is a tendency favouring rupture of the protein layer as it dries. After three dippings, *i.e.* after the deposition of 6 layers on each side of the gauze, most of the holes of the mesh were covered with protein when the gauze was dried and after collapse the protein subsides in visible sheets across

¹ Blodgett, *J.A.C.S.*, 1935, **57**, 1007.

the four corners of practically all the remaining holes of the mesh. Further dipping seems to close all the holes and to cover most of the tears seen in the first few layers. Occasional dust particles get drawn on to the gauze with the protein if any have chanced to settle on the protein film on the trough: since drying at room temperature takes some $\frac{1}{2}$ hour it is difficult to use one film for successive dippings and maintain it absolutely free from dust. The building of multilayers on silk fabric was difficult to follow under the microscope owing to the swelling and shrinking of the silk on wetting and drying which made the wet silk opaque.

The behaviour of protein multilayers deposited on gauze is to be contrasted with that of multilayers of esters and acids on gauzes described by Bikerman.² The latter layers burst as the drop occluded in the mesh of the gauze dried and the layers eventually formed micro-crystals or gels on the wires of the gauze. The protein monolayers are more elastic and, owing to association between the protein units, can stretch instead of breaking down and thus can span the gauze mesh with a thin layer even when they dry and shrink.

Naturally occurring lipoids and proteins can be spread at the air-water interface. When the jelly has been removed from newt or frog eggs the exposed egg cytolises completely at the air-water interface to form a typical lipoprotein monolayer. The newt egg cytolises more readily on distilled water than the frog egg; the former gives solid films with triolein pistons and the latter liquid films. Both of these lipoprotein films can be built up into multilayers. The spread newt egg or baby newt deposited on a chromium plated strip of metal in the form of a multilayer when X-rayed gave a spacing corresponding to 9.6 Å (a typical protein spacing) both in the first and second order. It also showed signs of a longer spacing of approximately 50 Å (a typical lipoidal spacing). The frog egg was deposited both on metal gauzes and on silk and gave beautiful interference colours on the former (where reflection from the "frame" occurs), but the holes in the mesh of the gauze were never covered by lipoprotein films. The films burst in the way described by Bikerman for films of lipid substances and irregular projections became visible on the wires of the gauze. The latter could not all have been due to dust and were presumably the remains of the broken films. Lipoprotein multilayers were also deposited on gauzes with meshes spanned by protein.

The gauzes with their deposited films were mounted with hot wax on to a glass plate through which a hole 3 mm. in diameter had been drilled and the region which had come in contact with or close to the hot wax was rendered impermeable with vaseline. The glass plate was then mounted by rubber washers between two half cells which could each be filled with suitable solutions. Electrical connection was made with each half cell to saturated calomel electrodes. In addition in all work with chloride solutions platinum wires dipping into the half cells were silver plated and chloridised to give Ag/AgCl electrode which could be used to measure the diffusion of Cl⁻ ions.

The resulting membranes were sufficiently impermeable to allow of no visible diffusion through the membrane during the space of one month of a saturated solution of isamine blue (in distilled water) into distilled water. This seems to be evidence that the tears that occurred sporadically throughout the micromembrane were mostly if not entirely covered by other layers of protein and that the layers were not permeable to the dye. The membranes used had approximately 200 layers.

Acetate-acetic acid buffers were tried but gave no appreciable diffusion potential due to the membrane (they gave the same potential as filter papers or no membrane between the two solutions) and on taking out the

² Bikerman, *Proc. Roy. Soc., A*, 1939, 170, 130.

glass plate from these solutions holes invariably were found in the protein membrane. These solutions therefore seemed to peptise the membranes.

Figures for the diffusion of aqueous NaCl, unbuffered and at pH from 5.4 to 6.4, showed that membranes of some 200 protein layers offered practically no resistance to the passage of NaCl as judged by the two Ag/AgCl electrodes which were 2.4 cm. apart and separated by the glass plate (some 1 cm. of diameter in the cells) which contained the membrane. The half lives of the potentials between these electrodes when $M/1$ NaCl was diffusing into $M/1000$ NaCl were not very reproducible and were 20 hours or more and were slightly shorter than would have been expected in the absence of the glass plate and membrane if diffusion alone was transporting the solutions into each other. The explanation of these results presumably is that convection was taking place, due to the different densities of different concentrations of the salt solution in the concentration gradient and to the presence both of stray vibrations and of diurnal variations in laboratory temperature. Owing to the non-homogeneous character of the membrane with its stray tears it was not thought profitable to attempt to get more accurate results.

The diffusion potentials across the membranes were initially + 27 to + 132 millivolts (strong solution positive) and fell towards the potential for the diffusion of $M/1$ into $M/1000$ NaCl, which, when observed directly or through a filter paper membrane, was + 22 millivolts when the calomels were uncorrected for liquid junction potentials. These liquid junction potentials were not set up very carefully and hence perhaps the discrepancy in the potentials initially observed. All the experiments agreed, however, in giving a half life of the decay of the potential to its ultimate value of some 20 minutes. No such decay was observed when filter paper membranes were used and the presence of some 40 layers of lipoprotein made no difference to the half life of the potential or to its value.

It appears therefore that 200 protein layers are sufficiently different from water, as regards their permeability to sodium and chloride ions, as to allow an appreciable membrane effect on the diffusion potential, but that they are so permeable to sodium chloride that the potential falls to that for diffusion in the absence of a membrane with a half life of 20 minutes in the presence of very slight convection in the two solutions in contact with it. The lipoprotein membranes, even when deposited on protein membranes, are too permeable even to affect the diffusion potential after 15 seconds, when the first measurements were made. Thus the lipoprotein probably breaks up into microcrystals or gel particles even on protein membranes; alternatively they form layers not strikingly different in permeability from the protein layers.

It seems evident, therefore, that protein multilayers of 200 molecules or less thick cannot maintain a diffusion potential with NaCl for any appreciable length of time; they could maintain a Donnan potential, but the latter is likely to be small in the presence of considerable quantities of sodium chloride and similar electrolytes. Thus bioelectrical potentials if maintained across thin protein layers need to have concentration gradients maintained across them by chemical means or by chemical means plus convection. Alternatively these potentials are maintained across membranes less permeable to electrolytes than protein multilayers and consist presumably of lipoids or of mosaics of lipid and protein with the latter occupying only a negligible fraction of the total surface.

It was also found that corrosion rates were unaffected by protein multilayers, which further supports the view of their being permeable to simple electrolytes.

Quantitative estimates as to the permeability, etc., of protein multilayers from the data obtained are of little value since the effects of convection are uncertain, and were not eliminated, and in any case the experimental data are not very reproducible except as to orders of magnitude. Diffusion equations for the case of no convection have been developed³ and these can be applied to the decay of the diffusion potentials. Assuming for 200 layers a mean thickness of 2000 Å it seems that the diffusion constant for NaCl in the membrane is 2.67×10^{-11} cm.² sec.⁻¹ as compared to 1.1×10^{-5} cm.² sec.⁻¹ in water. All the membranes tested gave values close to this for the thickness assumed. With triolein pistons each layer might well be thicker than one monolayer so that the diffusion constant is likely to be greater than the figure given. Assuming the thickness of 2000 Å and hence that $D = 2.67 \times 10^{-11}$ cm.² sec.⁻¹ the partition coefficient obtained for the electrolyte between water and the membrane obtained from the diffusion equations showed the electrolyte to be less soluble in the protein than in the water in a ratio that varied between the limits 1.56 to 1 and 31.2 to 1. If the membrane was thicker than 2000 Å so that D was greater than 2.67×10^{-11} , then the ratios of 31.2 (or 1.56) to 1 should be increased to higher values to 1 in the ratio of the square root of the diffusion constant. Denoting the diffusion potential due to the membrane as $k \log_{10} c/c_1$, where c and c_1 are the concentrations on its two sides, k varied from $\frac{5}{8}$ to 36, but values for k are unreliable owing to the variability, in these experiments, of the liquid-liquid junction potentials between M/1000 NaCl and the saturated calomel cell. None of the above figures can be considered in any way truly quantitative, but they give a general idea of the properties of these layers. The results seem to show that diffusion constants for NaCl through protein multilayers are less than through water, that electrolyte is less soluble in the multilayer than in water, and that protein multilayers can exert diffusion potentials in the case of NaCl. None of these conclusions are unexpected.

Summary.

Stable protein multilayers can be stretched across fine mesh wire gauzes and silk. The resulting films are impermeable to isamine blue but sufficiently permeable to NaCl for 200 monolayers to hold a diffusion potential different to that in the absence of membrane at a value which decays with a half life of 20 minutes. Interposing some 40 layers of spread amphibian eggs between the protein layers does not appreciably affect the properties of the membranes which were somewhat variable. It appears that the diffusion constant of NaCl is lower in the membrane than in water and that the partition coefficient leads to lower salt concentrations in the membrane. Amphibian eggs when spread give lipoprotein films, some of whose spacings can be determined from X-ray data.

The authors would like to express their thanks to Professor Rideal, F.R.S., for advice and for the interest he has taken throughout the course of this work and to Dr. R. B. Dean for assistance in dipping frames.

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³ Gatty (*in the press*).

REVIEWS OF BOOKS.

Lange's Handbook of Chemistry. Third edition, 1939. (Handbook Publishers, Inc., Sandusky, Ohio. Pp. 1850. Price \$6.)

Dr. Lange and the publishers have been well advised, costly though it must have been, to issue this new edition after an interval of only 2 years. The great value of this very inexpensive, but particularly well produced book lies in that it is up-to-date. The revision of the atomic weight of hydrogen has necessitated the recalculation of a large number of figures.

The present edition contains 42 pages more information, the new matter including an expansion from 7 to 24 pages of the "definitions" of chemical and physical terms and new tables on the properties of cast metals and of photographic emulsions, and on the reduction of barometric readings to sea level as well as a list of dimensional formulæ. A summary of the Joint Committee's recommendations for symbols for thermo- and physico-chemical quantities is also included, although a few pages later the editors have not yet accustomed themselves to its use, *e.g.*, in giving the van't Hoff isochore, which provides a pretty exercise in the use of *italic*, *Clarendon italic*, and roman type!

The reviewer has found the previous editions exceedingly useful and this one seems even better.

An Introduction to the Principles of Physical Chemistry. By O. MAASS and E. W. R. STEACIE. Second Edition. (New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd., 1939. Pp. ix + 395. 15s.)

The first edition of this book appeared in 1931, and was intended as an introduction to physical chemistry for chemists, chemical engineers and students of medicine and the biological sciences. There have been many minor changes made in the preparation of this new edition, and new chapters have been added dealing with atomic structure, the phase rule and colloids. The chapter on electrolytic dissociation has been modified, and a short section on the Debye-Hückel theory added. The treatment of electrochemistry has been greatly extended and the chapter on the rates of chemical reactions has been entirely rewritten. Another valuable new feature is the inclusion of a large number of questions and problems on the subject-matter of each chapter.

The book in its present form should prove very useful as a text for elementary classes. Its most outstanding feature is the modern approach adopted by the authors, coupled with their emphasis on fundamentals. It is not often, for example, that one finds an adequate discussion of the Langmuir theory of adsorption or of homogeneous and heterogeneous catalysis in an elementary book. The authors have included these and many similar topics, and have, moreover, discussed them in a way which would give the beginner a good grasp of the underlying principles. The book should give an admirable basis for more advanced courses. The

only general criticism which may be raised is that the price is too high for it to be used generally by students. This is the more regrettable since a work of such high standard could do much to raise the standard of instruction in elementary physical chemistry in schools and universities.

H. J. E.

Electro-Acoustics. By ERWIN MEYER. (London: Bell. Pp. xi and 117, with 12 plates. Price 10s.)

This book is rather obviously a printing of five lectures which the author delivered in London in 1937. Interesting they undoubtedly were, and they attracted large audiences, but in this permanent form they are less satisfactory and show some lack of balance, with a tendency to emphasis on aspects which would seem particularly to interest the lecturer. Special attention is, perhaps not unnaturally, paid (almost to the extinction of other work) to ideas coming from the author's own country. The value the book might have had as a permanent record for future consultation is minimised by the absence of an index.

Cumming and Kay's Textbook of Quantitative Analysis, viith edition by F. C. GUTHRIE and J. T. NANCE. (London: Gurney and Jackson. Pp. xv + 496. 15s. net.)

This book is too well known to need lengthy review. There is considerable new matter; in particular, in the section on electrometric titrations, which is admirable, the revisers have added a useful note on oxidation-reduction titrations; in addition, methods are given for the determination of some of the less common elements and for the determination of W, Mo, V and Cr in steel.

The volume is, as usual, excellently produced.

Theoretical Electrochemistry. By N. A. MCKENNA, B.A. Macmillan, 1938. 469 pp. 15s.

This book has evidently been constructed from abstracts made by the author of numerous papers on electrochemistry. On the whole, the author has chosen the right papers, and he has abstracted most of them rather well, but the manner in which these abstracts have been thrown together to form this book is lamentable. The absence of continuity in the book indicates that the author lacks familiarity with the subject, and has failed to grasp it as a coherent whole. The attempt to give a reasoned account of transport phenomena *before* discussing equilibrium properties is doomed to failure. Some of the digressions into thermodynamics are particularly confusing, and the author's ideas about osmotic pressure are, to say the least, antiquated.

While not to be recommended for teaching purposes, this book may be found useful for reference purposes by those already familiar with the modern aspects of electrochemistry.

E. A. G.

Kurzes Lehrbuch der physikalischen Chemie. Vol. II. By Professor KARL JELLINEK. (Deventer, Holland; A. E. Kluwer, 1939. Pp. xii + 292, with 149 Figs. and 29 Tables. Price 7.50 Fl.)

This book is Part II of Professor Jellinek's short textbook of Physical Chemistry and deals with the subjects of Electrochemistry, Phase Rule, Surface Chemistry (and Colloids) and Reaction Kinetics. The present volume is in itself a complete work, and although the index is reserved for the final volume, there is a detailed summary of the contents.

The topics are divided into four sections; the first, occupying more than half of the book, summarises the purely electrical properties of solution of electrolytes and includes a chapter on molten salts. The second section, on the phase rule, deals only with systems of one and two components. The third section, on surface chemistry, is very comprehensive and includes accounts of surface films, adsorption from solutions, electric double layers, colloid chemistry, and an excellent chapter on the kinetics and thermodynamics of the formation of a new phase. The last section treats of reaction kinetics and includes a lucid account of the kinetics of electrode processes.

The book as a whole is well balanced; theory and fundamental proofs are explained in detail and much space has been given to short but sufficiently detailed descriptions of experimental methods. The working out of some hundred problems in the text appeals to the reviewer as a novel way of presenting the subject.

This is not an elementary book, but can be recommended as a textbook for advanced students and teachers of physical chemistry.

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